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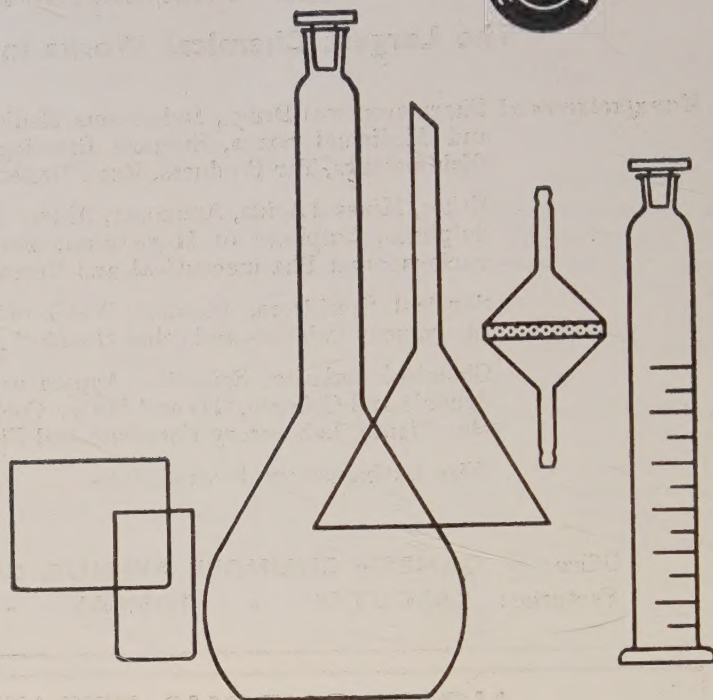
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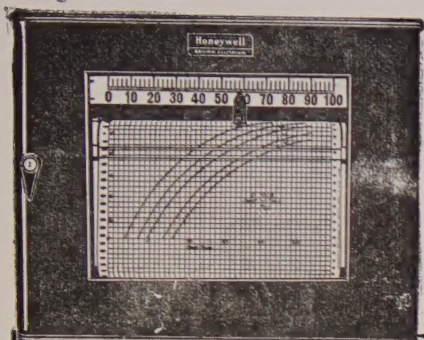
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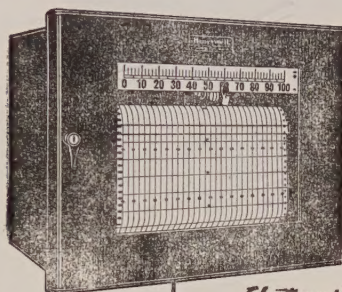


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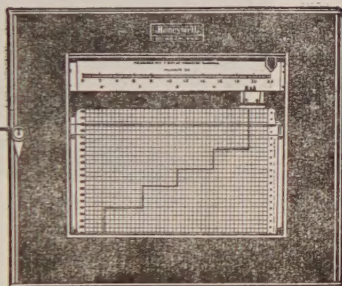
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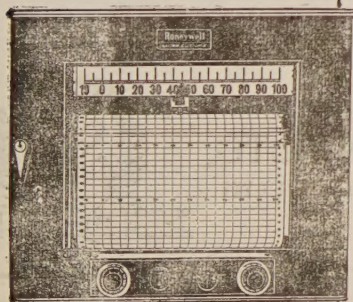
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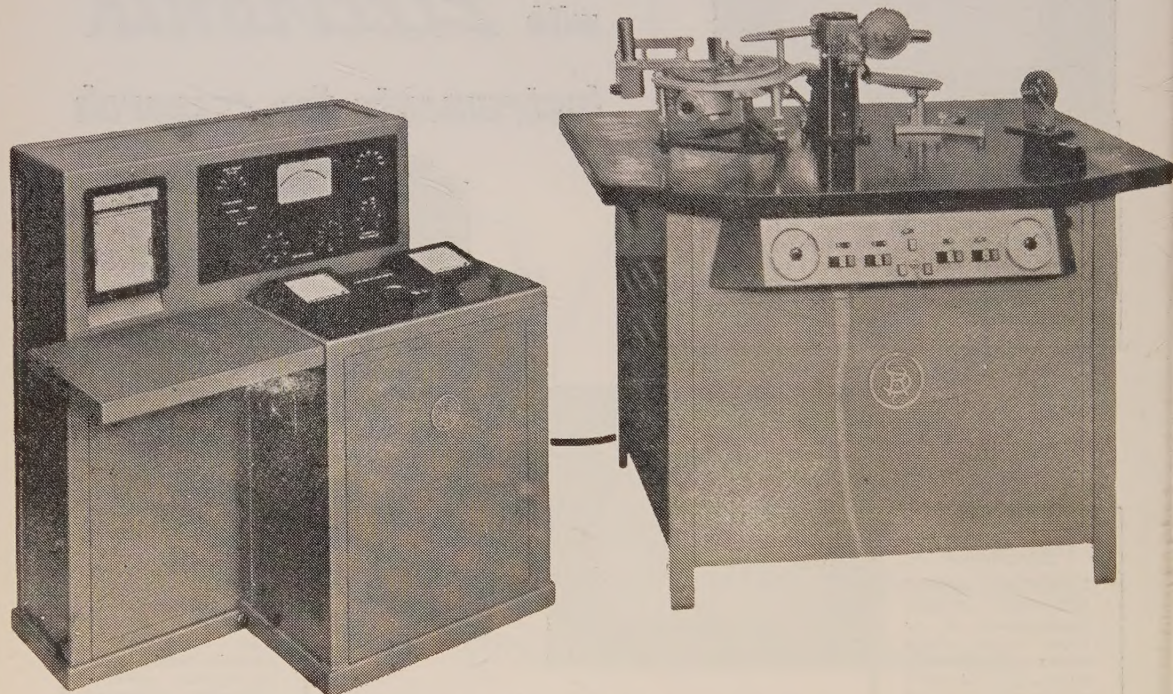
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THERMODYNAMIC PROPERTIES OF FLUID FLOW ACROSS A MAGNETIC FIELD

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ABSTRACT. This paper deals with the study of the various thermodynamic quantities like internal energy, enthalpy, entropy, etc., involved in the investigation of the flow of a conducting fluid in the presence of a uniform transverse magnetic field. The analogues of Rayleigh and Fanno lines readily follow from the basic equations. It is shown that the internal energy and enthalpy of an electrically conducting fluid obeying perfect gas depends, in the presence of a transverse magnetic field, on its density and the strength of the magnetic field. The entropy and the specific heat at constant volume do not seem to be affected by the presence of the magnetic field. The behaviour of the specific heat at constant pressure depends on which of the gas pressure and the total pressure is kept constant. A transverse magnetic field reduces the specific heat at constant gas pressure and the corresponding adiabatic constant by a factor proportional to the ratio of the magnetic pressure to the gas pressure. However, if the total pressure is kept constant, the magnetic field has no effect on the specific heat. Lastly, the effect of the magnetic field on the velocity of sound is discussed. In the limiting cases of weak and strong magnetic fields, the velocity of sound reduces to the ordinary sonic speed and the Alfvén speed respectively.

I. INTRODUCTION

The hydrodynamical motion of an electrically conducting fluid in the presence of a transverse magnetic field gives rise to induced electric currents which interact with the magnetic field to produce mechanical forces thereby affecting the fluid flow. Therefore, it is necessary to take account of this hydromagnetic interaction, and hence, the terms involving magnetic field appear in the equations governing the fluid flow (Alfvén, 1950; and Hoffmann and Teller, 1950). The investigation of the compressible fluid flow in the presence of a transverse magnetic field was initiated by Hoffmann and Teller (1950) who described the relativistic and nonrelativistic propagation of plane hydromagnetic shock waves in a medium of infinite electrical conductivity.

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In order to take account of the contribution of the magnetic field to the pressure and internal energy of the fluid, we define total pressure p^x and total internal energy E^x as

$$p^x = p + \frac{H^2}{8\pi} \quad \dots (1)$$

and

$$E^x = E + \frac{H^2}{8\pi\rho} \quad \dots (2)$$

The unstarred quantities p and E refer to the gas pressure and internal energy in the absence of the magnetic field H . These quantities are connected by the relation

$$E = \frac{1}{\gamma-1} \frac{p}{\rho} \quad \dots (3)$$

In terms of the total pressure p , the total internal energy E^x is given by

$$E^x = \frac{1}{\gamma-1} \left(\frac{p^x}{\rho} \right) + \frac{\gamma-2}{\gamma-1} \left(\frac{H^2}{8\pi\rho} \right) \quad \dots (4)$$

where γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume.

Similarly, the total enthalpy h^x may be defined as

$$h^x = E^x + \frac{p^x}{\rho} = h + \frac{H^2}{4\pi\rho} \quad \dots (5)$$

where h is the enthalpy in the absence of the magnetic field.

In terms of the Alfvén speed

$$V_{Af} = \left(\frac{H^2}{4\pi\rho} \right)^{\frac{1}{2}} \quad \dots (6)$$

the expression for total enthalpy h^x becomes

$$h^x = h + V_{Af}^2 \quad \dots (7)$$

From the equations obtained for the limiting case of infinitesimal disturbances in the Hoffmann-Teller paper (1950), we may write the equations governing the thermodynamics of hydromagnetic fluid flow as the following:

The equation of continuity or constant mass flux

$$\rho v = \text{constant} = M \quad \dots (8)$$

the equation of constant momentum flux

$$\rho v^2 + p^x = \overline{p^x} \quad \dots (9)$$

and the equations

$$\frac{1}{2}v^2 + h^x = \overline{h^x} \quad \dots (10)$$

and

$$Hv = \text{constant} \quad \dots (11)$$

where $\overline{p^x}$ and $\overline{h^x}$ are the stagnation values of total pressure and total enthalpy. Eq. (10) is analogous to the first law of thermodynamics, while the Eq. (11) describes the relation of magnetic field strength and gas velocity v . From Eqs. (8) and (11) it follows that

$$\frac{H}{\rho} = \text{constant} = \alpha \quad (12)$$

In other words, the changes in magnetic field strength and density are such that the strength of the magnetic field is always proportional to density.

II. RAYLEIGH AND FANNO LINES

The elimination of v between Eqs. (8) and (9) yields

$$p^x + \frac{M^2}{\rho} = p + \frac{H^2}{8\pi} + \frac{M^2}{\rho} = \overline{p^x} \quad \dots (13)$$

which is the analogue of the Rayleigh line in ordinary gasdynamics.

Similarly, the elimination of v between (8) and (10) gives

$$h^x + \frac{1}{2} \left(\frac{M}{\rho} \right)^2 = h + \frac{H^2}{4\pi\rho} + \frac{1}{2} \left(\frac{M}{\rho} \right)^2 = \overline{h^x} \quad \dots (14)$$

which is analogous to the customary Fanno line.

On expressing H in terms of ρ with the help of Eq. (12), these equations reduce to

$$p + \frac{\alpha^2}{8\pi} \rho^2 + \frac{M^2}{\rho} = \overline{p^x} \quad \dots (15)$$

and

$$h + \frac{\alpha^2}{4\pi} \rho + \frac{1}{2} \left(\frac{M}{\rho} \right)^2 = \overline{h^x} \quad \dots (16)$$

The constant α is determined from the initial value of the magnetic field and gas density when the gas is at rest.

III. CHANGE IN INTERNAL ENERGY

From Eq. (2) we have for the change in internal energy

$$dE^x = d \left(E + \frac{H^2}{8\pi\rho} \right)$$

which, with the help of Eq. (12), reduces to

$$dE^x = dE + \frac{H^2}{8\pi\rho^2} d\rho \quad \dots \quad (17)$$

For a gas satisfying the perfect gas law

$$p = RT\rho \quad \dots \quad (18)$$

with R and T as the universal gas constant and absolute temperature, the change in internal energy is given by

$$\left(\frac{\partial E^x}{\partial \rho} \right)_T = \left(\frac{\partial E}{\partial \rho} \right)_T + \frac{H^2}{8\pi\rho^2} = \frac{1}{2} \left(\frac{V_{Ay}^2}{\rho} \right) \quad \dots \quad (19)$$

where V_{Ay} is the Alfvén speed. In the limit of zero magnetic field

$$\left(\frac{\partial E^x}{\partial \rho} \right)_T \rightarrow \left(\frac{\partial E}{\partial \rho} \right)_T = 0$$

Hence, the internal energy of a perfect gas of infinite electrical conductivity in the presence of a transverse magnetic field depends—unlike in the thermodynamics of ordinary fluid flow—on its density.

IV. CHANGE IN ENTHALPY

Similarly, on combining Eqs. (5) and (12), we have for the change in enthalpy

$$\begin{aligned} dh^x &= d \left(h + \frac{H^2}{4\pi\rho} \right) \\ &= dh + d \frac{H^2}{4\pi\rho^2} d\rho \quad \dots \quad (20) \end{aligned}$$

For a gas obeying Eq. (18), the last equation yields

$$\left(\frac{\partial h^x}{\partial \rho} \right)_T = \frac{H^2}{4\pi\rho^2} = \frac{V^2_{Ay}}{\rho} \quad \dots \quad (21)$$

and for $H \rightarrow 0$,

$$\left(\frac{\partial h^x}{\partial \rho} \right)_T \rightarrow \left(\frac{\partial h^x}{\partial \rho} \right)_T = 0$$

Therefore, it may be concluded that, like internal energy, the enthalpy also depends on the density of a conducting fluid in the presence of a transverse magnetic field.

V. CHANGE IN ENTROPY

Here it will be shown that the terms involving magnetic field do not appear in the expression for the change in entropy (Sen, 1956)

$$ds^x = \frac{dQ^x}{T} = \frac{1}{T} \left[dE^x + p^x d \left(\frac{1}{\rho} \right) \right] \quad \dots \quad (22)$$

because, on substitution for p^x and dE^x from Eqs. (1) and (17), we have

$$\begin{aligned} ds^x &= \frac{1}{T} \left[dE + \frac{H^2}{8\pi\rho^2} d\rho + p d \left(\frac{1}{\rho} \right) - \frac{H^2}{8\pi\rho^2} d\rho \right] \quad \dots \quad (23) \\ &= \frac{1}{T} \left[dE + p d \left(\frac{1}{\rho} \right) \right] = \frac{dQ}{T} \\ &= ds \end{aligned}$$

VI. SPECIFIC HEATS OF GAS

The specific heat of the fluid at constant volume is given by

$$C^x_{vol.} = \left(\frac{\partial E^x}{\partial T} \right)_{vol.} = \left(\frac{\partial E}{\partial T} \right)_{vol.} = C_{vol.} \quad \dots \quad (24)$$

Therefore, the specific heat at constant volume is not affected by the magnetic field.

The influence of a transverse magnetic field on the specific heat at constant pressure depends, however, on which of the gas pressure p or the total pressure p^x is kept constant. If the gas pressure p is kept constant, then

$$C^x_p = \left(\frac{\partial h^x}{\partial T} \right)_p = C_p + \frac{H^2}{4\pi p^2} \left(\frac{\partial p}{\partial T} \right)_p \quad \dots \quad (25)$$

which, for a perfect gas, becomes

$$C_p^x = C_p - 2R \left(\frac{H^2}{8\pi\rho} \right)$$

$$\text{or} \quad C_p^x - C_p = -2R \frac{\text{Magnetic pressure}}{\text{Gas pressure}} \quad \dots (26)$$

Hence, the presence of a transverse uniform magnetic field reduces, in this case, the specific heat at constant gas pressure by an amount proportional to the ratio of the magnetic pressure and the gas pressure.

In the second case, when the total pressure p^x is kept constant, we similarly have

$$\begin{aligned} C_{p^x}^x &= \left(\frac{\partial h^x}{\partial T} \right)_{p^x} = \left[\frac{\partial}{\partial T} \left\{ E + \frac{p^x}{\rho} + \frac{H^2}{8\pi\rho} \right\} \right]_{p^x} \\ &= C_{vol} + p^x \frac{\partial}{\partial T} \left(\frac{1}{\rho} \right)_{p^x} + \frac{H^2}{8\pi\rho^2} \left(\frac{\partial \rho}{\partial T} \right) \quad \dots (27) \\ &= C_{vol} + p^x \frac{\partial}{\partial T} \left(\frac{1}{\rho} \right), \end{aligned}$$

[by virtue of Eq. (12)]

$$= C_p$$

In this case, the terms involving magnetic field do not appear in the expression for the specific heat which has the same value as in the nonmagnetic case. Similarly, the adiabatic constant of the gas is influenced by the transverse magnetic field if the gas pressure is maintained constant.

VII. LOCAL VELOCITY OF SOUND

The new velocity of sound C^x is analogically defined with the help of Eqs. (1) and (12), as

$$C^x = (C^2 + V_{Af}^2)^{\frac{1}{2}} \quad \dots (28)$$

where C is the velocity of sound in the absence of the magnetic field. In the case of magnetic field, the new velocity of sound in a conducting fluid is increased, the increment being proportional to the ratio of the magnetic pressure and the gas

pressure. However, if the magnetic field exceeds the gas pressure considerably, the new velocity of sound approaches the Alfvén speed. The coincidence with the Alfvén speed is purely accidental. Although the sound waves appear to have precisely the same velocity as that of Alfvén waves, they are longitudinal in character whereas the Alfvén waves are transverse in nature. Similarly, the Mach number, in the case of very strong magnetic fields, is defined by the ratio of the flow speed and the Alfvén speed.

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Sen, H. K., 1956, *Phys. Rev.*, **102**, 5.

SCATTERING OF ELECTRONS BY A SCREENED COULOMB FIELD IN HIGHER BORN APPROXIMATION

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(Received March 28, 1961)

ABSTRACT. The relativistic scattering of electrons by heavy atoms has been studied by taking the Rozental approximation of the Thomas-Fermi potential. The differential cross section of scattering has been calculated in the Born approximation up to second order in the expansion of $\frac{Ze^2}{\hbar v}$. The numerical results of the scattering of electrons of energy 150 KeV at an angle 90° have been given for the elements, argon, krypton, xenon and mercury.

INTRODUCTION

We propose to study the scattering of the fast electrons by heavy atoms. For high energy scattering the potential of the atom is usually taken as that due to the nuclear charge alone, the screening effects of the atomic electrons being neglected. It is, however, worth while to investigate the effects of screening due to the atomic electrons on electron scattering. The Hartree-Fock method which takes good account of the screening in the potential function is suitable only for light atoms, considering the practical difficulties involved. For heavy atoms the treatment of the screened potential by the statistical method of Thomas-Fermi is more practicable. Unfortunately there is no analytic expression for the Thomas-Fermi potential. Various approximate representations of the Thomas-Fermi potential are cited in the literature (Majewsky and Tietz, 1957). Among them the Rozental form which is a combination of three potentials of Yukawa type with different weight factors, is suitable for analytic treatment in higher Born approximations. With this potential the differential cross section for electron scattering up to second order has been calculated. Numerical results are given for the elements argon ($Z = 18$), krypton ($Z = 36$), xenon ($Z = 54$) and mercury ($Z = 80$) at 150 KeV incident electron energy. These are compared with the corresponding numerical results for the Coulomb potential without screening. The differential scattering cross section are expressed as the ratio of $d\sigma$ to $d\sigma_R$ where $d\sigma_R$ is the well-known Rutherford scattering cross section.

RESULTS AND DISCUSSION

Taking relativistic units $\hbar = c = m = 1$, the Dirac equation can be written as

$$[E - i(\alpha \cdot \nabla) + \beta]\psi = -Ze^2 V\psi$$

$$V = \frac{1}{r}\phi(r) = \frac{1}{\mu x} [0.255e^{-0.246x} + 0.581e^{-0.947x} + 0.164e^{-4.356x}]$$

where

$$x = \frac{r}{\mu}, \quad \mu = \frac{1}{4} \left(\frac{9\pi^2}{2Z} \right)^{1/3} a_0, \quad a_0 = \text{First Bohr radius}$$

Following Vachaspati (1954), the expression for the scattering cross section in Born approximation up to second order can be written as

$$d\sigma = d\sigma_1 + d\sigma_2$$

where
$$d\sigma_1 = 4(Z\alpha)^2 |a_1|^2 k^2 \cos^2\theta/2 \left(1 + \frac{1}{k^2} \sec^2\theta/2 \right)$$

$$d\sigma_2 = 16(Z\alpha)^3 a_1 E k^2 \cos^2\theta/2 \left[(a_{3r} + \frac{1}{2}a_{2r}) + \frac{1}{k^2} a_{2r} \sec^2\theta/2 \right]$$

$$a_1 = \frac{1}{4\pi} (\mathbf{k}_1 | V | \mathbf{k}_0), \quad \mathbf{k}_0 = \text{initial momentum}, \quad \mathbf{k}_1 = \text{final momentum}$$

$$|\mathbf{k}_0| = |\mathbf{k}_1| = k$$

$$a_{2r} = \frac{1}{4\pi(2\pi)^3} P \int \frac{(\mathbf{k}_1 | V | \mathbf{k}')(\mathbf{k}' | V | \mathbf{k}_0)}{k'^2 - k^2} d^3k'$$

$$= \frac{4\pi}{(2\pi)^3} \sum_{i < j=1}^3 \frac{\alpha_i \alpha_j}{k^3} M_3(\lambda_i, \lambda_j) + \frac{4\pi}{(2\pi)^3} \sum_{i=1}^3 \frac{\alpha_i^2}{k^3} M_3(\lambda_i, \lambda_i)$$

$$a_{3r} = \frac{1}{4\pi(2\pi)^3(n, P)} P \int \frac{(\mathbf{k}_1 | V | \mathbf{k}')(n \cdot \mathbf{k}')(\mathbf{k}' | V | \mathbf{k}_0)}{k'^2 - k^2} d^3k'$$

$$= \frac{4\pi}{(2\pi)^3 P^2} \sum_{i < j=1}^3 \left\{ \frac{4k^2 + \lambda_i^2 + \lambda_j^2}{k^3} M_3(\lambda_i, \lambda_j) + \frac{2}{k} M_2(\lambda_i, \lambda_j) - I_i - I_j \right\} \alpha_i \alpha_j$$

$$+ \frac{4\pi}{(2\pi)^3 P^2} \sum_{i=1}^3 \left\{ \frac{2k^2 + \lambda_i^2}{k^3} M_3(\lambda_i, \lambda_i) + \frac{1}{k} M_2(\lambda_i, \lambda_i) - I_i \right\} \alpha_i^2$$

M_2 and M_3 are given by Lewis (1956) and quoted in the Appendix.

$$\alpha_1, \alpha_2, \alpha_3 = 0.255, 0.581, 0.164; \quad \lambda_1, \lambda_2, \lambda_3 = 0.246, 0.947, 4.356.$$

The Rutherford scattering cross section is $d\sigma_R = \frac{(Ze^2)^2}{4} \frac{1-\beta^2}{\beta^4 \sin^4 \theta/2}$. The value of k for 150 KeV incident electron energy is 0.820534 and the ratios $d\sigma_1/d\sigma_R$ and $d\sigma_2/d\sigma_R$ are given by

$$\frac{d\sigma_1}{d\sigma_R} = \frac{2k^4(k^2+2)}{(k^2+1)} |a_1|^2$$

$$\frac{d\sigma_2}{d\sigma_R} = 8Ze^2 a_1 E \frac{k^6}{k^2+1} \left[a_{3r} + \left(0.5 + \frac{2}{k^2} \right) a_{2r} \right]$$

TABLE I

| Z | $d\sigma_1/d\sigma_R$ | | $d\sigma_2/d\sigma_R$ | | $d\sigma/d\sigma_R$ | |
|----|-----------------------|----------|-----------------------|----------|---------------------|----------|
| | Coulomb | Rozental | Coulomb | Rozental | Coulomb | Rozental |
| 18 | 0.798815 | 0.796772 | 0.054211 | 0.061621 | 0.853026 | 0.858393 |
| 36 | 0.798815 | 0.795642 | 0.108422 | 0.127284 | 0.907237 | 0.922926 |
| 54 | 0.798815 | 0.794643 | 0.162634 | 0.194867 | 0.961449 | 0.989510 |
| 80 | 0.798815 | 0.793438 | 0.240939 | 0.294507 | 1.039754 | 1.087945 |

In Table I, the value of $\frac{d\sigma_1}{d\sigma_R}$ i.e., the ratio of the first order relativistic scattering cross section calculated with the Rozental potential and the Coulomb potential, to the Rutherford cross section (non-relativistic Coulomb scattering cross section) are given at 150 KeV incident electron energy for different values of the atomic number Z . Correspondingly, the ratio $\frac{d\sigma_2}{d\sigma_R}$, shows the contribution of the second order term only in the scattering cross section and finally there is a column for $d\sigma/d\sigma_R$ which is equal to $\frac{d\sigma_1 + d\sigma_2}{d\sigma_R}$. It is found that $d\sigma_1/d\sigma_R$ for the Rozental potential is slightly less (e.g. about 0.5% less for $Z = 54$) than the corresponding ratio for Coulomb potential; the difference between the two ratios increases as Z increases. This is quite in agreement with the expectation that the screening should decrease the scattering cross section, though the very small difference between the two ratios indicates that the effect of screening is not appreciable at this energy. It is interesting to note, however, that the ratio for the Rozental potential is considerably larger than the corresponding ratio for the Coulomb potential (e.g. about 20% larger for $Z = 54$). We can obtain $d\sigma_2$ for the Coulomb potential from the Rozental potential, after putting $\lambda_i = 0$, $i = 1, 2, 3$ and $\alpha_i = \alpha_j = 0$, $\alpha_k = 1$, then a_{2r} reduce to zero in this limit, and a_{3r} gives a non-zero value which correctly reduces $d\sigma_2$ for the Rozental case to the corresponding

expression for the Coulomb case. In the Rozental case, however, the contribution to the cross section from the terms associated with a_{2r} is not negligible; in fact it is found to be about twenty per cent of the contributions due to the other terms.

APPENDIX

In our calculations we have utilised the following expressions given by Lewis (1956):

$$Re M_2(\mu, \nu) = Re\{k \int d^3k' [(K_1^2 + \mu^2)(K_2^2 + \nu^2)]^{-1}\} = \frac{2\pi^2 k}{K} \arctan \left[\frac{K}{\mu + \nu} \right]$$

$$Re M_3(\mu, \nu) = Re\{k^3 \int d^3k' [(k'^2 - k^2 - i\epsilon)(K_1^2 + \mu^2)(K_2^2 + \nu^2)]^{-1}\} \\ = \pi^2 k^3 [k^2(K^2 + \mu^2 + \nu^2)^2 - \rho^2 \mu^2 \nu^2]^{-\frac{1}{2}}$$

$$\left\{ \arctan \left[\frac{k[K^2 + (\mu + \nu)^2] + [k^2(K^2 + \mu^2 + \nu^2)^2 - P^2 \mu^2 \nu^2]^{-\frac{1}{2}}}{\mu \nu (\mu + \nu)} \right] \right. \\ \left. - \arctan \left[\frac{k[K^2 + (\mu + \nu)^2] - [k^2(K^2 + \mu^2 + \nu^2)^2 - P^2 \mu^2 \nu^2]^{-\frac{1}{2}}}{\mu \nu (\mu + \nu)} \right] \right\}$$

$$Re M_3(\mu, \mu) = 2\pi^2 k^3 \{[k^2 K^2 + 4k^2 \mu^2 + \mu^4]^{-\frac{1}{2}} / K\} \times \\ \arctan \{K \mu [k^2 K^2 + 4k^2 \mu^2 + \mu^4]^{-\frac{1}{2}}\}$$

$$Re I_i = Re\{ \int d^3k' [(K_1^2 + \lambda_i^2)(k'^2 - k^2 - i\epsilon)]^{-1} \} = \frac{\pi^2}{k} \arctan \frac{2k}{\lambda_i} \text{ with.}$$

$$K = \mathbf{k}_i - \mathbf{k}_f = \mathbf{k}_0 - \mathbf{k}_1; P = \mathbf{k}_0 + \mathbf{k}_1; K_1 = \mathbf{k}_0 - \mathbf{k}'; K_2 = \mathbf{k}' - \mathbf{k}_1.$$

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FLUORESCENCE SPECTRA OF SOME URANYL SALTS

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Plate IV (A and B) Plate V (A and B)

ABSTRACT. The fluorescence spectra of uranyl acetate, nitrate, sulphate, fluoride I, chloride, potassium uranyl sulphate and ammonium uranyl sulphate have been reinvestigated at room and liquid air temperatures and new analyses have been proposed for each spectrum on the basis of a single electronic allowed transition.

INTRODUCTION

The fluorescence spectra of uranyl compounds are studied in detail by many workers since the first investigations were made by Becquerel (1872) and Becquerel and Onnes (1909). In our earlier paper (Rao and Narasimham, 1956), a comprehensive review of the available literature on the spectroscopic properties of the uranyl salts was given. It was shown that the earlier analyses of Freymann (1946) and Pant (1945, 1950) were open to question in several respects. The most satisfactory analysis of the compounds has been proposed by Dieke and Duncan (1949) but they gave analysis for the spectra of only two salts—caesium uranyl nitrate and caesium uranyl chloride. Therefore investigations are again carried out on uranyl acetate ($2\text{H}_2\text{O}$), nitrate ($6\text{H}_2\text{O}$), sulphate ($3\text{H}_2\text{O}$), chloride ($1\text{H}_2\text{O}$), fluoride I (XH_2O), potassium sulphate ($2\text{H}_2\text{O}$) and ammonium sulphate ($2\text{H}_2\text{O}$) at room and liquid air temperatures and new analyses have been proposed for the fluorescence bands of each compound on the basis of a single electronic transition with one upper state and one lower state. In the case of ammonium uranyl sulphate, the analysis of the fluorescence bands has been proposed for the first time.

EXPERIMENTAL

The experimental set-up for fluorescence consists of a brass rod with a circular slot of 5 cm. depth in the middle in which a small glass tube containing the investigating salt in fine powder form is placed tightly. The brass rod has three small holes bored at the middle of the slot (2.5 cm. from the top) two in one line to allow the incident light on the substance from two mercury arcs on opposite sides and the third perpendicular to the line joining the above two. This allows the fluorescence from the substance into the spectrograph.

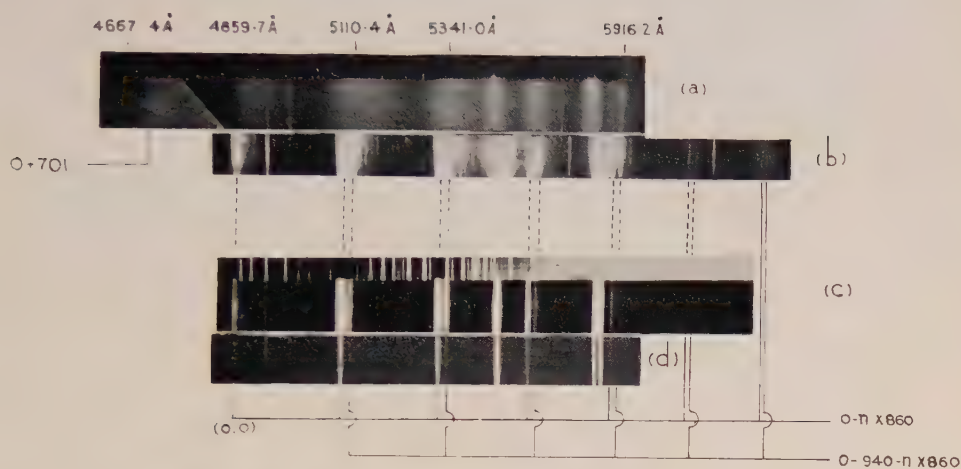


Fig. 1. Fluorescence spectra of uranyl acetate

- (a) At room temperature.
- (b) At liquid air temperature (exposure 1 hour).
- (c) At liquid air temperature (exposure 20 minutes).
- (d) At liquid air temperature (exposure 5 minutes).

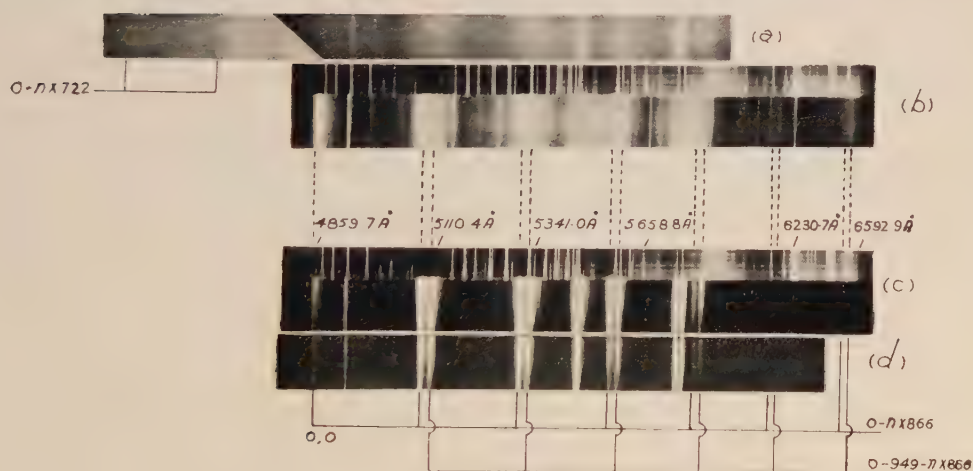


Fig. 2. Fluorescence spectra of uranyl nitrate

- (a) At room temperature.
- (b) At liquid air temperature (exposure 1 hour).
- (c) At liquid air temperature (exposure 20 minutes).
- (d) At liquid air temperature (exposure 5 minutes).

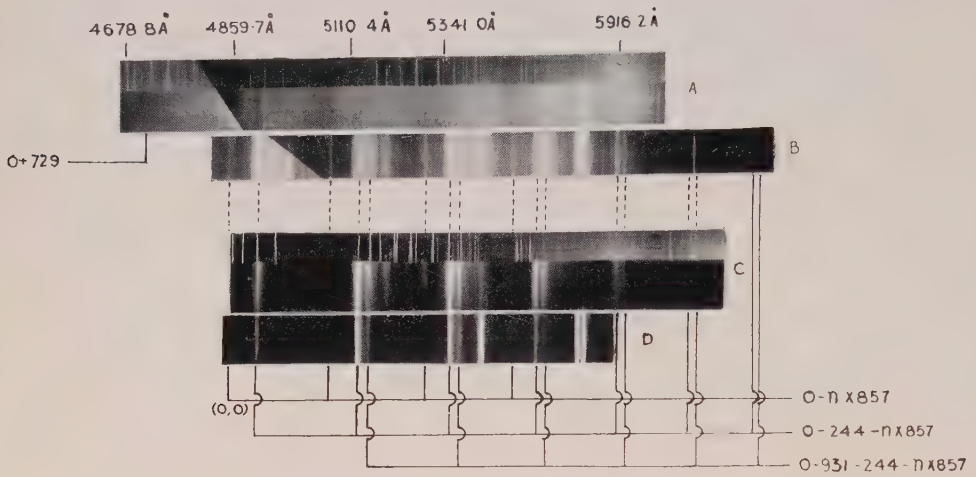


Fig. 3. Fluorescence spectra of uranyl sulphate

- (a) At room temperature.
- (b) At liquid air temperature (exposure 1 hour).
- (c) At liquid air temperature (exposure 20 minutes).
- (d) At liquid air temperature (exposure 5 minutes).

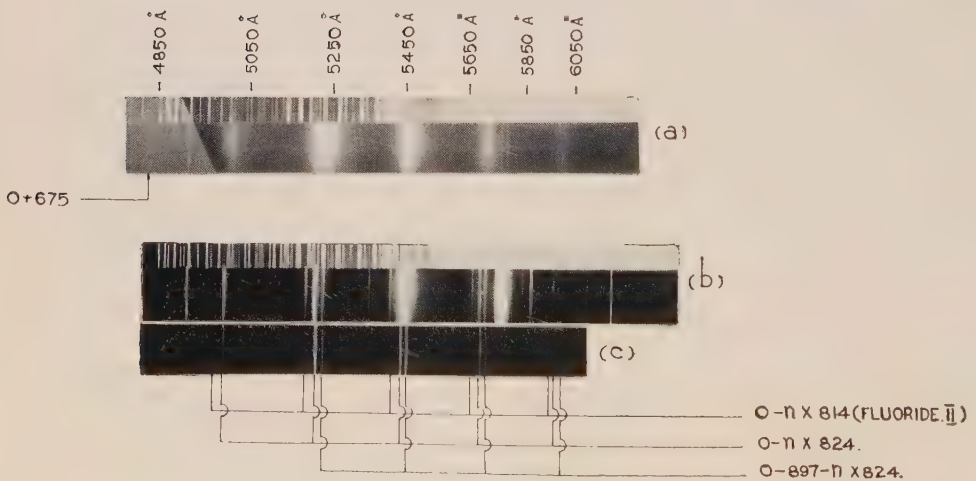


Fig. 4. Fluorescence spectra of uranyl fluoride I

- (a) At room temperature.
- (b) At liquid air temperature (long exposure).
- (c) At liquid air temperature (short exposure).

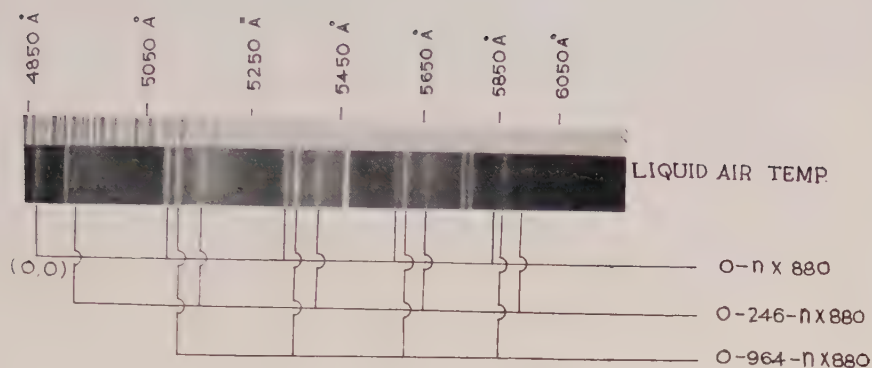


Fig. 5. Fluorescence spectrum of uranyl chloride

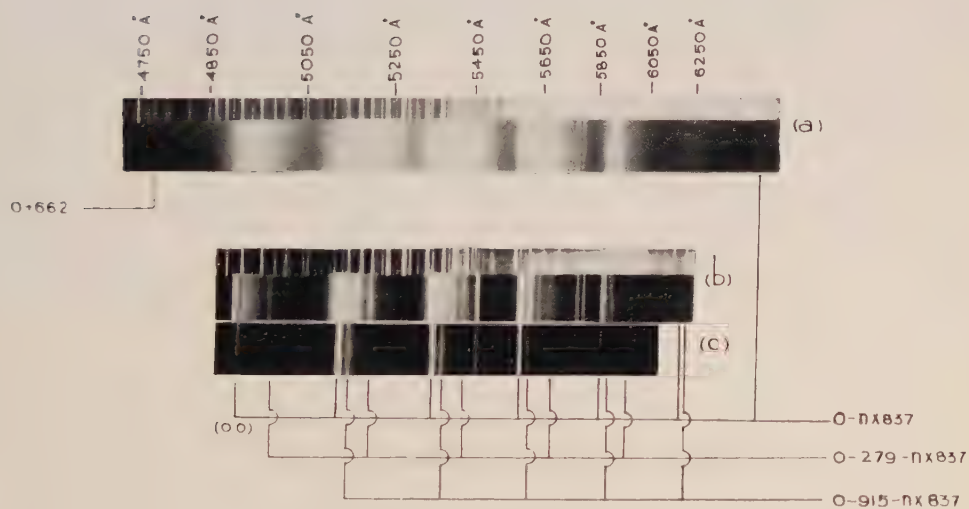


Fig. 6. Fluorescence spectra of potassium uranyl sulphate

- (a) At room temperature.
- (b) At liquid air temperature (long exposure).
- (c) At liquid air temperature (short exposure).

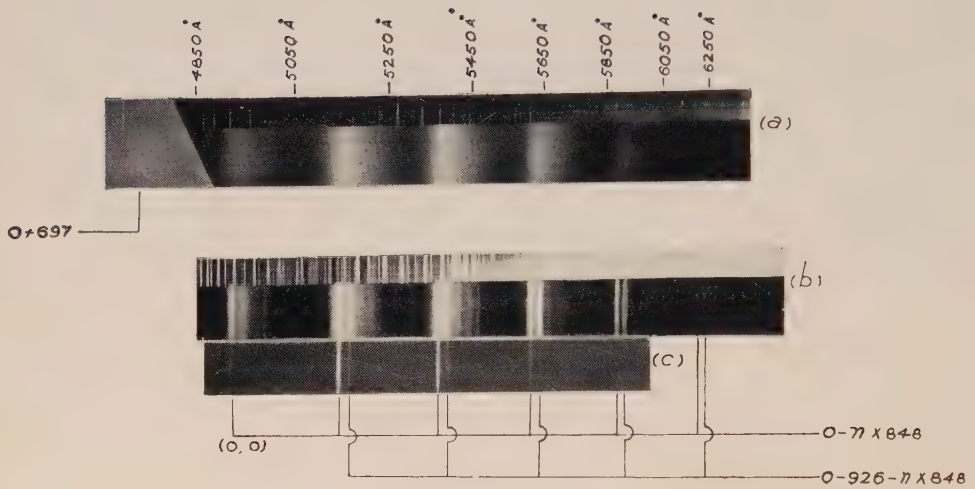


Fig. 7. Fluorescence spectra of ammonium uranyl sulphate

- (a) At room temperature.
- (b) At liquid air temperature (long exposure).
- (c) At liquid air temperature (short exposure).

A special type of quartz Dewar flask (supplied by Thermal Syndicate Ltd.) is used as the container for the liquid air to study the fluorescence spectra at liquid air temperature. The Dewar flask has three fused plane windows on each wall. The holes in the brass rod could be aligned parallel to these windows. The brass rod is suspended by means of a wire into the liquid air contained in the Dewar flask. The specimen under investigation was found to acquire a temperature of -177°C . The spectrum is photographed on a Fuess spectrograph (dispersion of 33 \AA/mm at 5000 \AA) using Ilford HP3 panchromatic plates.

With this set-up, exposures are given ranging from a few minutes to one hour. A very intense picture with even the weakest bands can be obtained in one hour exposure while five minute's exposure is sufficient to bring out the principal bands of the spectrum.

The fluorescence spectra are taken at liquid air and room temperatures. In all cases, mercury arcs are used as sources of exciting radiations and glass filters having a low transmission value from the blue green to higher wavelengths are used to eliminate the mercury lines in the fluorescence region. The bands are measured against standard iron arc lines. The accuracy of measurements for the sharp bands is 2 cm^{-1} , 5 cm^{-1} for moderate diffuse bands and 15 cm^{-1} for very diffuse bands. The intensities given are visual estimates from the spectrograms in the 1 to 10 scale and the following abbreviations are adopted for the description of the bands.

| | |
|------------------|-----------------|
| vsh—very sharp | d—diffuse |
| sh—sharp | vd—very diffuse |
| msh—medium sharp | |

RESULTS AND DISCUSSION

The fluorescence spectra of the uranyl acetate, nitrate, sulphate, chloride, fluoride I, potassium sulphate and ammonium sulphate at liquid air and room temperatures with different exposure times are reproduced in Figs. 1 to 7, Plates IV and V. At room temperature, new bands which are diffuse, are recorded in the region of absorption corresponding to the upper state fundamental of the symmetric stretching frequency of the uranyl ion. At liquid air temperature, a few additional bands extending the previous data, are also recorded in the case of uranyl acetate, nitrate and sulphate.

The bands, in general, form into about seven or eight groups separated by about 860 cm^{-1} corresponding to the symmetric stretching frequency of the UO_2 ion in the ground state. In all the spectra except that of fluoride I, we find the strong doublet pattern of bands repeating at regular intervals with the long wavelength member of each pair weaker than the shorter wavelength component. In the case of fluoride I a strong triplet pattern of bands repeats at regular intervals. In between the groups, a number of weaker bands are observed.

Earlier analyses :

Pant (1945) studied the fluorescence spectra of uranyl acetate, sulphate, chloride, fluoride I, fluoride II and potassium uranyl sulphate and analysed the bands of each spectrum on the basis of two electronic transitions with two close lying ground states and a common upper state. Freymann and co-workers (1946, 1947) published another analysis of the fluorescence bands of uranyl acetate, nitrate, chloride and fluoride II. They interpreted the bands on the basis of a forbidden transition with a very weak or totally absent band as (0,0) (Pant's A_0 band). The defects of both these two types of analyses have been discussed at length in our earlier paper (Rao and Narasimham, 1956).

Present analysis

The fluorescence bands of each substance have been analysed on the basis of a single electronic allowed transition (Table I to VII). The important features in the analysis of each compound are given below.

Uranyl acetate

The (0,0) band in the fluorescence spectrum of the acetate is fixed at 20587 cm^{-1} . The reasons for this choice are

- (i) This band is strong both in fluorescence and absorption.
- (ii) In fluorescence, this is the first strong band on the short wavelength side.
- (iii) At room temperature, a fluorescence band is obtained at 21288 cm^{-1} , with a shift of 701 cm^{-1} from this band alone and the frequency corresponds to the upper state fundamental of the symmetric stretching vibration of the uranyl ion, recorded in absorption.
- (iv) In absorption experiments, two pairs of emission bands have been recorded on the long wavelength side of the (0,0) band agreeing with the first two strong pairs of fluorescence bands. These emission bands could be interpreted as $0\cdot n \times 860$ and $0\cdot 940\cdot n \times 860$ with the (0,0) band at 20587 cm^{-1} (Narasimham and Rao, 1960).

Out of the 57 bands in acetate, about 46 bands could be interpreted on the basis of four fundamentals in the ground state 860 (U—O symmetric stretching), 940 (U—O asymmetric stretching), 222 (O—U—O symmetric bending) and 36 cm^{-1} (crystal lattice vibration) and three frequencies in the upper state 701, 210 and 33 cm^{-1} (see Table I). The band at 19968 cm^{-1} is taken as due to the fundamental 599 characteristic of the acetate radical. This suggestion is only a possibility adopted from Dieke's (1949) observation that, in acetates, a fundamental of about 600 cm^{-1} is generally observed.

Uranyl nitrate

For the same reasons as in acetate, the strong band at 20582 cm^{-1} has been

chosen as the (0,0) band. Out of a total 60 bands, 51 bands could be interpreted on the basis of four fundamentals in the ground state 866 cm^{-1} (U—O symmetric stretching), 949 cm^{-1} (U—O asymmetric stretching) 222 cm^{-1} (symmetric bending) and 31 cm^{-1} (crystal lattice frequency) and three fundamentals in the upper state 722 cm^{-1} (corresponding to 860 cm^{-1} in the ground state), 210 and 33 cm^{-1} (Table II). The band at 20028 cm^{-1} is interpreted as due to a fundamental 554 cm^{-1} . Two more such bands are observed in the next groups. A possible suggestion is that this may be a fundamental of the nitrate radical.

Uranyl sulphate

The fixing up of the (0, 0) band in the sulphate spectrum is a problem of special interest. At liquid air temperature the first prominent band in fluorescence is at 20316 cm^{-1} .

TABLE I
Fluorescence bands of uranyl acetate

| Wave-number of the band cm^{-1} | Inten-sity | Shift from (0,0) band ($\Delta\nu$) | Assignment | | |
|--|------------|---------------------------------------|-------------------|---------------------------------|---------------------------|
| | | | Present author | Freyman (1947) | Pant (1945) |
| (1) | (2) | (3) | (4) | (5) | (6) |
| 21288** | 2 vd | + 701 | 0+701=701 | | |
| 20739*? | 1 d | + 152 | | (0,0) | A ₀ |
| 20620* | 1 msh | + 33 | 0+33=33 | | |
| 20587* | 8 sh | | (0,0) | 0+720-860 | B ₀ |
| 20551 | 3 msh | - 36 | 0-36=36 | | |
| 20463 | 2 sh | - 124 | | | |
| 20426 | 3 sh | - 161 | | 0+2×720-2×860 | D ₀ |
| 20365 | 2 sh | - 222 | 0-222=222 | 0+720-860-210 | B ₀ -235 |
| 20270 | 2 sh | - 317 | | 0+720-930-210 | A ₀ -2×235 |
| 20146 | 3 sh | - 441 | 0-2×222=444 | 0+720-860-2×210 | B ₀ -2×235 |
| 20112 | 2 sh | - 475 | 0-36-2×222=480 | | |
| 20059 | 1 sh | - 528 | | | |
| 19988 | 1 sh | - 599 | 0-599=599 | | |
| 19874 | 2 sh | - 713 | 0+210-940=730 | 0-860 | A ₀ -855 |
| 19808 | 1 msh | - 778 | | | |
| 19763 | 2 msh | - 824 | 0+33-860=827 | | |
| 19727*** | 10 sh | - 860 | 0-860=860 | 0+720-2×860 | B ₀ -855 |
| 19683 | 3 d | - 904 | 0-36-860=896 | | |
| 19647*** | 6 sh | - 940 | 0-940=940 | 0+720-860-930 | A ₀ -855-235 |
| 19618 | 2 d | - 969 | 0-36-940=976 | | |
| 19556 | 3 sh | -1031 | | 0+720-2×930 or 0+2×720-3×860 | D ₀ -855 |
| 19509 | 3 sh | -1078 | 0-222-860=1082 | 0+720-2×860-210 | B ₀ -855-235 |
| 19461 | 3 sh | -1126 | 0-36-222-860=1118 | | |
| 19411 | 3 sh | -1176 | | 0+720-860-930 -210 | A ₀ -855-2×235 |
| 19366 | 1 d | -1221 | | | B ₀ -855-2×235 |

TABLE I (Contd.)

| Wave-number of the band cm^{-1} | Intensity | Shift from (0,0) band ($\Delta\nu$) | Assignment | | |
|--|-----------|---------------------------------------|---|---|--|
| | | | Present author | Freyman (1947) | Pant (1945) |
| (1) | (2) | (3) | (4) | (5) | (6) |
| 19312] | 2 d | -1275] | $0 - 2 \times 222 - 860 = 1304$ | | |
| 19255] | 2 d | -1332] | | | |
| 19168 | 1 msh | -1419 | | | |
| 19107 | 2 msh | -1480 | | | |
| 19020 | 2 sh | -1567 | | $0 - 2 \times 860$ | $A_0 - 2 \times 855$ |
| | | | $= 1590$ | | |
| 18898 | 1 d | -1689 | $0 + 33 - 2 \times 860 = 1687$ | | |
| 18866*** | 10 sh | -1721 | $0 - 2 \times 860 = 1720$ | $0 + 720 - 3 \times 860$ | $B_0 - 2 \times 855$ |
| 18789*** | 8 sh | -1798 | $0 - 940 - 860 = 1800$ | $0 + 720 - 2 \times 860 - 930$ | $A_0 - 2 \times 855 - 235$ |
| 18746 | 2 msh | -1841 | $0 - 36 - 940 - 860 = 1836$ | | |
| 18705 | 2 sh | -1882 | | $0 + 720 - 860 - 2 \times 930$ or $0 + 2 \times 720 - 2 \times 860$ | $D_0 - 2 \times 855$ |
| 18664 | 2 sh | -1923 | $0 - 222 - 2 \times 860 = 1942$ | $0 + 720 - 3 \times 860$ | |
| 18608 | 2 sh | -1979 | | | $B_0 - 2 \times 855 - 235$ |
| 18552 | 2 sh | -2035 | | $0 + 720 - 2 \times 860 - 930$ $- 210$ | $A_0 - 2 \times 855$ $- 2 \times 235$ |
| 18412 | 1 d | -2175 | $0 - 2 \times 222 - 2 \times 860$ $= 2164$ | | |
| 18153 | 1 msh | -2434 | $0 + 210 - 940 - 2 \times 860$ $= 2450$ | $0 - 3 \times 860$ | $A_0 - 3 \times 855$ |
| 18009 | 8 sh | -2578 | $0 - 3 \times 860 = 2580$ | $0 + 720 - 4 \times 860$ | $B_0 - 3 \times 855$ |
| 17982 | 2 msh | -2605 | $0 - 36 - 3 \times 860 = 2616$ | | |
| 17926 | 6 sh | -2661 | $0 - 940 - 2 \times 860 = 2660$ | $0 + 720 - 3 \times 860 - 930$ | $A_0 - 3 \times 855 - 235$ |
| 17895 | 1 d | -2692 | $0 - 36 - 940 - 2 \times 860$ $= 2696$ | | |
| 17802 | 2 d | -2785 | | | |
| 17771 | 1 msh | -2816 | $0 - 222 - 3 \times 860 = 2802$ | | $B_0 - 3 \times 855 - 235$ |
| 17678 | 1 d | -2909 | | $0 + 720 - 3 \times 860 - 930$ $- 210$ | $A_0 - 3 \times 855$ $- 2 \times 235$ |
| 17147 | 6 sh | -3440 | $0 - 4 \times 860 = 3440$ | $0 + 720 - 5 \times 860$ | |
| 17072 | 4 sh | -3515 | $0 - 940 - 3 \times 860 = 3520$ | $0 + 720 - 4 \times 860 - 930$ | |
| 17053 | 1 msh | -3534 | $0 - 36 - 940 - 3 \times 860$ $= 3556$ | | |
| 17005 | 2 d | -3582 | | | |
| 16482 | 1 d | -4105 | | | |
| 16303 | 1 d | -4284 | | | |
| 16273 | 3 sh | -4314 | $0 - 5 \times 860 = 4300$ | $0 + 720 - 6 \times 860$ | |
| 16205 | 2 sh | -4382 | $0 - 940 - 4 \times 860 = 4380$ | $0 + 720 - 5 \times 860 - 930$ | |
| 16091 | 1 msh | -4496 | $0 - 222 - 5 \times 860 = 4522$ | | |
| 15439 | 2 sh | -5148 | $0 - 6 \times 860 = 5160$ | | |
| 15392 | 2 sh | -5195 | $0 - 940 - 5 \times 860 = 5240$ | | |

* These bands are recorded in absorption also.

** This band is obtained at room temperature.

*** These bands are obtained in absorption as emission bands.

TABLE II
Fluorescence bands of uranyl nitrate

| Wave number of the band cm^{-1} | Intensity | Shift from (0,0) band | Assignment | |
|--|-----------|-----------------------|------------------------------------|---|
| | | | Present author | Frey mann (1947) |
| (1) | (2) | (3) | (4) | (5) |
| 22001** | 1 vd | +1419 | $0+2 \times 722=1444$ | |
| 21304** | 2 vd | + 722 | $0+722=722$ | |
| 20618* | 1 d | + 36 | $0+36=36$ | |
| 20582* | 8 sh | | (0,0) | $0+720-860$ |
| 20551 | 3 msh | - 31 | $0-31=31$ | |
| 20523 | 1 d | - 59 | $0-2 \times 31=62$ | |
| 20440 | 3 msh | - 142 | | |
| 20392 | 2 sh | - 190 | $0+36-222=186$ | $0+720-860-230$ |
| 20360 | 2 sh | - 222 | $0-222=222$ | |
| 20114 | 2 msh | - 468 | $0-2 \times 222=444$ | |
| 20028 | 1 msh | - 554 | $0-554=554$ | |
| 19924 | 3 sh | - 658 | $0+210-866=656$ | $0+720-860-3 \times 230$ |
| 19887 | 3 sh | - 695 | $0-31+210-866=687$ | |
| 19823 | 2 d | - 759 | $0+210-949=739$ | $0-930$ |
| 19762 | 2 d | - 820 | $0+36-866=830$ | |
| 19716*** | 10 sh | - 866 | $0-866=866$ | $0+720-2 \times 860$ |
| 19683 | 3 d | - 899 | $0-31-866=897$ | |
| 19633*** | 6 sh | - 949 | $0-949=949$ | $0+720-860-930$ or $0-860-230$ |
| 19588 | 2 d | - 994 | $0-31-949=980$ | |
| 19545 | 2 msh | -1037 | | $0+720-2 \times 860-930$ or $0-930-230$ |
| 19505 | 3 sh | -1077 | $0-222-866=1088$ | |
| 19455 | 3 sh | -1127 | $0-31-222-866=1119$ | $0+720-860-930-230$ |
| 19316 | 2 d | -1266 | $0-2 \times 222-866=1310$ | $0+720-2 \times 860-2 \times 230$ |
| 19225 | 2 d | -1357 | | $0+720-860-930-2 \times 230$ |
| 19160 | 1 d | -1422 | $0-554-866=1420$ | |
| 19057 | 3 msh | -1525 | $0+210-2 \times 866=1522$ | $0+720-2 \times 860-3 \times 230$ |
| 18965 | 2 msh | -1617 | $0+210-949-866=1605$ | $0-860-930$ |
| 18854*** | 8 sh | -1728 | $0-2 \times 866=1732$ | $0+720-3 \times 860$ |
| 18827 | 2 d | -1755 | $0-31-2 \times 866=1763$ | |
| 18777*** | 8 sh | -1805 | $0-949-866=1815$ | $0+720-2 \times 860-930$ or $0-2 \times 860-230$ |
| 18733 | 2 d | -1844 | $0-31-949-866=1846$ | |
| 18688 | 2 msh | -1894 | | $0+720-3 \times 860-230$ or $0-860-930-230$ |
| 18635 | 2 sh | -1947 | $0-222-2 \times 866=1954$ | $0+720-2 \times 860-930-230$ |
| 18593 | 2 msh | -1989 | $0-31-222-2 \times 866=1984$ | |
| 18562 | 1 msh | -2020 | | |
| 18530 | 1 msh | -2052 | | |
| 18494 | 1 d | -2088 | | $0+720-3 \times 860-2 \times 230$ |
| 18412 | 2 d | -2170 | $0-2 \times 222-2 \times 866=2176$ | |
| 18185 | 1 d | -2397 | $0+210-3 \times 866=2388$ | |
| 18105 | 1 d | -2477 | | $0-2 \times 860-930$ |

TABLE II (contd)

| Wave number of the band cm^{-1} | Intensity | Shift from (0,0) band | Assignment | |
|--|-----------|-----------------------|--------------------------------------|---|
| | | | Present author | Freymann (1947) |
| (1) | (2) | (3) | (4) | (5) |
| 17984 | 6 sh | -2598 | $0-3 \times 866 = 2598$ | $0+720-4 \times 860$ |
| 17916 | 6 sh | -2666 | $0-949-2 \times 866 = 2681$ | $0+720-3 \times 860-930$ or $0-3 \times 860-230$ |
| 17803 | 2 d | -2779 | | |
| 17770 | 2 msh | -2812 | $0-222-3 \times 866 = 2820$ | $0+720-3 \times 860-930-230$ |
| 17726 | 2 msh | -2856 | $0-31-222-3 \times 866 = 2850$ | |
| 17501 | 2 d | -3081 | $0-2 \times 222-3 \times 866 = 3042$ | $0+720-3 \times 860-930$ -2×230 |
| 17458 | 1 d | -3124 | $0-554-3 \times 866 = 3152$ | |
| 17199 | 1 d | -3383 | $0+210-949-3 \times 866 = 3337$ | |
| 17137 | 4 sh | -3445 | $0-4 \times 866 = 3464$ | $0+720-5 \times 860$ |
| 17042 | 4 sh | -3540 | $0-949-3 \times 866 = 3547$ | $0+720-4 \times 860-930$ or $0-4 \times 720-230$ |
| 17011 * | 2 msh | -3571 | $0-31-949-3 \times 866 = 3578$ | $0+720-5 \times 860-230$ or $0-3 \times 860-930-230$ |
| 16898 | 2 msh | -3684 | $0-222-4 \times 866 = 3686$ | $0+720-4 \times 860-930-230$ |
| 16629 | 2 d | -3953 | $0-2 \times 222-4 \times 866 = 3908$ | $0+720-860-930+2 \times 230$ |
| 16267 | 3 sh | -4315 | $0-5 \times 866 = 4330$ | $0+720-6 \times 860$ |
| 16193 | 3 sh | -4389 | $0-949-4 \times 866 = 4413$ | $0+720-5 \times 860-930$ or $0-5 \times 860-230$ |
| 16045 | 2 msh | -4537 | $0-222-5 \times 866 = 4552$ | |
| 15900 | 1 d | -4682 | | |
| 15780 | 1 d | -4802 | $0-2 \times 222-5 \times 866 = 4774$ | |
| 15438 | 2 msh | -5144 | $0-6 \times 866 = 5196$ | $0+720-7 \times 860$ |
| 15362 | 2 d | -5220 | $0-949-5 \times 866 = 5279$ | $0-6 \times 860-230$ |

* These bands are recorded in absorption also.

** These bands are observed at room temperature.

*** These bands are recorded in absorption as emission bands.

However, at the same temperature but with longer exposures, a less prominent band develops at 20560 cm^{-1} . The frequency shift between these two is 244 cm^{-1} . The values for these bands in absorption are 20317 and 20561 cm^{-1} respectively. But the band at 20561 cm^{-1} is much stronger than that at 20317 cm^{-1} . It is possible to understand this intensity variation if we assume the (0, 0) band to be at 20560 cm^{-1} and interpret the 20316 cm^{-1} as $0-244$ (ν_2 bending frequency). In the fluorescence spectra of many organic molecules the (0, 0) band is extremely weak compared with some of the fundamentals due to the phenomenon of self-absorption. A similar process may be considered as responsible for the weakness of this (0, 0) band in fluorescence (20560 cm^{-1}).

The analysis of the sulphate spectrum (Table III) presents some unique features. The actual fundamentals are 857 , 931 , 244 and 25 cm^{-1} in the ground state of the uranyl ion and 729 , 242 and 32 cm^{-1} in the upper state. In the

acetate and nitrate spectra, the frequency 222 cm^{-1} represented by a weak band whereas in the sulphate, this frequency 244 cm^{-1} has a high intensity. All strong bands of the spectrum could be interpreted only in terms of combination with this fundamental. It is clear that this fundamental 244 plays an important role in the fluorescence spectrum. Another fundamental 962 cm^{-1} is assigned as a possible sulphate ion frequency.

Sevchenko and Stepanov (1949) studied the infra red absorption of the sulphate and observed frequencies forbidden for a linear model of the uranyl ion. Therefore, they concluded that the uranyl ion is bent in sulphate. The fact that the bending frequency 244 cm^{-1} is very strong in the fluorescence spectrum of the sulphate is a further justification for the idea that the uranyl ion is bent in sulphate.

TABLE III
Fluorescence bands of uranyl sulphate

| Wave number of the band cm^{-1} | Intensity | Shift from (0,0) band cm^{-1} obs. value | Assignment |
|--|-----------|--|--------------------------------------|
| (1) | (2) | (3) | (4) |
| 21289** | 2 vd | + 729 | $0 + 729 = 729$ |
| 21066** | 1 vd | + 506 | |
| 20560* | 1 sh | | (0,0) |
| 20442* | 1 sh | - 118 | |
| 20379* | 2 sh | - 181 | $0 + 2 \times 32 - 244 = 180$ |
| 20348* | 2 sh | - 212 | $0 + 32 - 244 = 212$ |
| 20316* | 7 vsh | - 244 | $0 - 244 = 244$ |
| 20291 | 3 vsh | - 269 | $0 - 25 - 244 = 269$ |
| 20262 | 2 sh | - 298 | $0 - 2 \times 25 - 244 = 294$ |
| 20228 | 1 sh | - 332 | |
| 20177 | 3 sh. | - 383 | |
| 20149 | 3 sh | - 411 | |
| 20124 | 1 sh | - 436 | |
| 20095 | 1 msh | - 465 | $0 + 32 - 2 \times 244 = 456$ |
| 20065*** | 3 sh | - 495 | $0 - 2 \times 244 = 488$ |
| 20040 | 2 msh | - 520 | $0 - 25 - 2 \times 244 = 513$ |
| 19987 | 1 msh | - 573 | $0 + 32 + 242 - 857 = 583$ |
| 19949 | 2 sh | - 611 | $0 + 242 - 257 = 615$ |
| 19929 | 1 msh | - 631 | $0 - 25 + 242 - 857 = 640$ |
| 19890 | 2 msh | - 670 | |
| 19864 | 1 msh | - 696 | |
| 19810 | 2 sh | - 750 | $0 - 3 \times 244 = 732$ |
| 19776 | 1 msh | - 784 | |
| 19703*** | 6 vsh | - 857 | $0 - 857 = 857$ |
| 19629 | 2 sh | - 931 | $0 - 931 = 931$ |
| 19598 | 1 msh | - 962 | $0 - 962 = 962$ |
| 19560 | 1 msh | -1000 | |
| 19521 | 3 msh | -1039 | $0 + 2 \times 32 - 244 - 857 = 1037$ |
| 19498 | 4 msh | -1062 | $0 + 32 - 244 - 857 = 1069$ |
| 19464*** | 10 vsh | -1096 | $0 - 244 - 857 = 1101$ |

TABLE III (contd.)

| Wave number of the band cm ⁻¹ | Intensity | Shift from (0,0) band cm ⁻¹ obs. value | Assignment |
|--|-----------|--|----------------------|
| (1) | (2) | (3) | (4) |
| 19430 | 2 sh | -1130 | 0-25-244-857=1126 |
| 19392 | 1 sh | -1168 | 0-2×25-931-244=1151 |
| 19372*** | 6 vsh | -1188 | 0-931-244=1175 |
| 19337 | 1 msh | -1223 | |
| 19316 | 2 sh | -1244 | |
| 19259 | 1 msh | -1301 | |
| 19216 | 2 sh | -1344 | 0-2×244-857=1345 |
| 19195 | 2 msh | -1365 | 0-25-2×244-857=1370 |
| 19111 | 1 msh | -1449 | 0+242-2×857=1472 |
| 19009 | 2 msh | -1551 | 0-3×244-857=1589 |
| 18910 | 1 msh | -1650 | |
| 18858 | 6 sh | -1702 | 0-2×857=1714 |
| 18787 | 1 msh | -1773 | 0-962-857=1819 |
| 18609*** | 10 vsh | -1951 | 0-244-2×857=1958 |
| 18574 | 2 sh | -1986 | 0-25-244-2×857=1983 |
| 18528*** | 8 vsh | -2032 | 0-931-244-857=2032 |
| 18465 | 2 msh | -2095 | |
| 18337 | 2 msh | -2223 | 0+2×244-2×857=2202 |
| 18243 | 2 msh | -2317 | 0+242-3×857=2329 |
| 18207 | 2 msh | -2353 | |
| 17992 | 4 vsh | -2567 | 0-3×857=2571 |
| 17924 | 1 d | -2636 | 0-962-3×857=2676 |
| 17759 | 8 vsh | -2801 | 0-244-3×857=2815 |
| 17671 | 6 vsh | -2889 | 0-931-244-2×857=2889 |
| 17576 | 2 msh | -2984 | |
| 17490 | 1 d | -3070 | 0-2×244-3×857=3059 |
| 17186 | 1 d | -3374 | |
| 17141 | 2 sh | -3419 | 0-4×857=3428 |
| 17024 | 1 sh | -3536 | 0-962-3×857=3533 |
| 16896 | 6 vsh | -3664 | 0-244-4×857=3672 |
| 16806 | 6 vsh | -3754 | 0-931-244-3×857=3746 |
| 16720 | 2 sh | -3840 | |
| 16613 | 1 msh | -3947 | 0-2×244-4×857=3916 |
| 16535 | 1 msh | -4025 | 0+242-5×857=4041 |
| 16378 | 1 d | -4182 | |
| 16171 | 1 msh | -4389 | 0-962-4×857=4390 |
| 16119 | 1 msh | -4441 | |
| 16061 | 2 sh | -4499 | 0-244-5×857=4529 |
| 15980 | 2 sh | -4580 | 0-931-244-4×857=4603 |
| 15908 | 1 msh | -4652 | |
| 15210? | 1 d | -5350 | 0-244-6×857=5386 |
| 15136? | 1 d | -5424 | 0-931-244-5×857=5460 |

* These bands are recorded in absorption also.

** These bands are obtained at room temperature.

*** These bands are recorded in absorption as emission bands.

Uranyl fluoride—I :

Out of the three fluorides i.e., anhydrous fluoride and two hydrated varieties called by Pant (1945) as fluoride I and fluoride II, fluoride I is the only compound which has shown fluorescence. The triplet pattern of bands observed in the fluorescence spectrum of fluoride I immediately makes us suspect whether this spectrum is entirely due to fluoride I or possibly due to any other fluoride that may exist as an impurity in fluoride I. On a comparison of the two bands at 20012 and 20092 cm^{-1} with those two observed in absorption of fluoride I and fluoride II, it was noted that the band at 20092 cm^{-1} in fluorescence can be attributed to fluoride II while the stronger band at 20012 cm^{-1} can be attributed to fluoride I. If we take these two as the (0, 0) bands for the two fluorides, all the bands could be explained on the basis of two series: Series I consisting of the comparatively weaker bands made out of the short-wavelength components of the triplet structure to be attributed to fluoride II and series II consisting of the central strong bands and the long wave length components of the triplet structures making the usual doublet patterns obtained in all other fluorescence spectra and interpreted on the same lines. This classification is indicated in fig. 4, Plate IV (B) and Table IV.

The shift between the two (0, 0) bands of the two fluorides is 80 cm^{-1} . The values of the symmetric stretching fundamental (ν_1) in fluoride I and fluoride II are respectively 824 and 814 cm^{-1} while the value of the asymmetric stretching frequency (ν_3) in fluoride I is 891 cm^{-1} . The ν_3 frequency of fluoride II may have about 70 cm^{-1} shift from the ν_1 and it makes its ν_3 fundamental and its combinations with the ν_1 fall on the ν_1 fundamental and its overtones of fluoride I. This might account for the singlet structure of the bands attributed to fluoride II.

TABLE IV
Fluorescence bands of uranyl fluoride I and II

| Wave-number of the band cm^{-1} | Intensity | Shift from (0,0) F. I | Shift from (0,0) F. II | Assignment | | Pant (1945) |
|--|-----------|-----------------------|------------------------|---------------------------|-------------|-----------------------|
| | | | | Present author Fluoride I | Fluoride II | |
| (1) | (2) | (3) | (4) | (5) | (6) | (7) |
| 20687* | 1 vd | + 675 | + 595 | 0+675=675 | | |
| 20092** | 4 vsh | + 80 | | | (0,0) | B ₀ |
| 20070** | 1 msh | + 58 | — 22 | | | |
| 20012** | 7 vsh | | — 80 | (0,0) | | A ₀ —176 |
| 19980 | 1 msh | — 32 | — 112 | 0—32=32 | | D ₀ |
| 19918 | 1 msh | — 94 | — 174 | | | B ₀ —176 |
| 19894 | 2 msh | — 118 | — 198 | | 0—198=198 | |
| 19812 | 1 msh | — 200 | — 280 | 0—200=200 | | D ₀ —176 |
| 19591 | 2 msh | — 421 | — 501 | 0—2×200=400 | | B ₀ —3×176 |
| 19489 | 1 msh | — 523 | — 603 | | | |

TABLE IV—(contd).

| Wave-number of the band cm ⁻¹ | Inten- sity | Shift from (0,0) F. I | Shift from (0,0) F. II | Assignment | | Pant (1945) |
|---|----------------|--------------------------------|---------------------------------|------------------------------|--------------------|---------------------------------|
| | | | | Present author Fluoride I | Fluoride II | |
| (1) | (2) | (3) | (4) | (5) | (6) | (7) |
| 19453 | 1 msh | — 559 | — 639 | | | |
| 19278*** | 6 vsh | — 734 | — 814 | | 0—814=814 | B ₀ —819 |
| 19188*** | 10 vsh | — 824 | — 904 | 0—824=824 | | A ₀ —827—176 |
| 19121*** | 7 vsh | — 891 | — 971 | 0—891=891 | | B ₀ —819—176 |
| 19085 | 1 msh | — 927 | —1007 | | 0—198—814 =1012 | |
| 18911 | 2 sh | —1101 | —1181 | 0—200—891=1091 | | A ₀ —827—2×176 |
| 18810 | 3 sh | —1202 | —1282 | 0—2×200—824 =1224 | | A ₀ —827—3×176 |
| 18763 | 2 msh | —1249 | —1329 | | | |
| 18726 | 1 msh | —1286 | —1366 | | | B ₀ —819—3×176 |
| 18639 | 3 sh | —1373 | —1453 | | | |
| 18574 | 1 msh | —1438 | —1518 | 0—3×200—824 =1424 | | |
| 18542 | 1 d | —1470 | —1550 | | | |
| 18502 | 1 d | —1510 | —1590 | | | A ₀ —2×827 |
| 18463*** | 5 vsh | —1549 | —1629 | | 0—2×814 =1628 | B ₀ —2×819 |
| 18405 | 2 sh | —1607 | —1687 | | | D ₀ —2×795 |
| 18363*** | 8 sh | —1649 | —1729 | 0—2×824=1648 | | A ₀ —2×827—176 |
| 18295*** | 6 sh | —1717 | —1797 | 0—891—824=1715 | | B ₀ —2×819—176 |
| 18154 | 1 msh | —1858 | —1938 | 0—200—2×824 =1848 | | B ₀ —2×795—176 |
| 18125 | 1 msh | —1887 | —1967 | | | |
| 18082 | 1 sh | —1930 | —2010 | 0—200—891—824 =1915 | | B ₀ —2×819 —2×176 |
| 18026 | 2 sh | —1986 | —2066 | | | |
| 17934 | 1 d | —2078 | —2158 | 0—2×200—2×824 =2048 | | B ₀ —3×819 —2×176 |
| 17657 | 3 sh | —2355 | —2435 | | 0—3×814 =2442 | B ₀ —3×819 |
| 17595 | 2 sh | —2417 | —2497 | | | B ₀ —3×795 |
| 17542 | 6 sh | —2470 | —2550 | 0—3×824=2472 | | A ₀ —3×827—176 |
| 17480 | 4 sh | —2532 | —2612 | 0—891—2×824 =2539 | | B ₀ —3×819—176 |
| 17191 | 2 d | —2821 | —2901 | | | |
| 17031 | 2 sh | —2981 | —3061 | | | |
| 16838 | 2 msh | —3174 | —3254 | | 0—4×814=3256 | |
| 16777 | 2 msh | —3235 | —3315 | | | |
| 16704 | 4 sh | —3308 | —3388 | 0—4×824=3296 | | |
| 16653 | 3 sh | —3359 | —3439 | 0—891—3×824 =3363 | | |
| 15913 | 1 msh | —4099 | —4179 | 0—5×824=4120 | | |
| 15855 | 1 msh | —4157 | —4237 | 0—891—4×824 =4187 | | |

* This band is recorded at room temperature.

** These bands are obtained in absorption also.

*** These bands are obtained as emission bands in absorption experiments.

The other fundamentals obtained in the fluorescence spectrum of fluoride I are the bending frequency of 200 cm^{-1} (ν_2), the crystal lattice frequency of 32 cm^{-1} in the ground state and 675 cm^{-1} of the ν_1 frequency in the upper state.

TABLE V
Fluorescence bands of uranyl chloride

| Wave-number of the band cm^{-1} | Intensity | Shift from (0,0) band | Assignment | | |
|--|-----------|-----------------------|-----------------------------------|---|-------------------|
| | | | Present author | Freymann (1947) | Pant (1945) |
| (1) | (2) | (3) | (4) | (5) | (6) |
| 20547* | 1 msh | + 26 | 0+26 | 0+720-875 | B_o |
| 20521* | 5 sh | | (0,0) | | |
| 20443* | 2 msh | - 78 | | 0+720-930 or 0-230 | A_o-246 |
| 20275 | 3 sh | - 246 | 0-246=246 | 0+720-875-230 | B_o-246 |
| 20213 | 2 d | - 308 | | 0+720-930-230 | |
| 20144 | 1 d | - 377 | | | $A_o-2\times 246$ |
| 19641 | 10 sh | - 880 | 0-880=880 | 0+720-2 \times 875 | B_o-876 |
| 19557 | 10 sh | - 964 | 0-964=964 | 0+720-875-930 or 0-875-230 | $A_o-876-246$ |
| 19391 | 5 sh | -1130 | 0-246-880=1126 | 0+720-2 \times 875-230 or 0-930-230 | $B_o-876-246$ |
| 19327 | 2 d | -1194 | 0-246-964=1210 | | |
| 19248 | 1 d | -1273 | | | |
| 18762 | 8 sh | -1759 | 0-2 \times 880=1760 | 0+720-3 \times 875 | |
| 18681 | 10 sh | -1840 | 0-964-880=1844 | 0+720-2 \times 875-930 or 0-2 \times 875-230 | |
| 18515 | 5 sh | -2006 | 0-246-2 \times 880=2006 | 0+720-3 \times 875-230 or 0-875-930-230 | |
| 18452 | 1 d | -2069 | 0-246-964-880=2090 | | |
| 18370 | 1 d | -2151 | | | |
| 17884 | 4 sh | -2637 | 0-3 \times 880=2640 | 0+720-4 \times 875 | |
| 17806 | 8 sh | -2715 | 0-964-2 \times 880=2724 | 0+720-4 \times 875-230 | |
| 17636 | 4 msh | -2885 | 0-246-3 \times 880=2886 | 0-2 \times 875-930-230 | |
| 17551 | 1 d | -2970 | 0-246-964-2 \times 880 =2970 | | |
| 16989 | 2 sh | -3532 | 0-4 \times 880=3520 | 0+720-5 \times 875 | |
| 16920 | 4 sh | -3601 | 0-964-3 \times 880=3604 | 0+720+4 \times 875-930 or 0-4 \times 875-230 | |
| 16755 | 1 d | -3766 | 0-246-4 \times 880=3766 | 0+720-5 \times 875-230 or 0-3 \times 875-930-230 | |

* These bands are obtained in absorption also.

TABLE VI
Fluorescence bands potassium uranyl sulphate

| Wave-number of the band cm^{-1} | Intensity | Shift from (0,0) band cm^{-1} | Assignment | |
|--|-----------|--|---|----------------------------|
| | | | Present author | Pant (1945) |
| (1) | (2) | (3) | (4) | (5) |
| 21035** | 1 vd | + 662 | $0 + 662 = 662$ | |
| 20476* | 1 d | + 103 | $0 + 3 \times 30 = 90$ | A_0 |
| 20431* | 2 sh | + 58 | $0 + 2 \times 30 = 60$ | |
| 20373* | 10 vsh | | (0,0) | B_0 |
| 20329* | 2 sh | - 44 | $0 - 44 = 44$ | |
| 20302* | 4 sh | - 71 | $0 - 2 \times 44 = 88$ | $A_0 - 172$ |
| 20263 | 2 sh | - 110 | | D_0 |
| 20241* | 3 sh | - 132 | | |
| 20211 | 3 sh | - 162 | | |
| 20179 | 2 msh | - 194 | $0 - 194 = 194$ | $B_0 - 172$ |
| 20148 | 1 msh | - 225 | | |
| 20094 | 6 sh | - 279 | $0 - 279 = 279$ | $A_0 - 2 \times 172$ |
| 20046 | 2 sh | - 327 | $0 - 44 - 279 = 323$ | $B_0 - 2 \times 172$ |
| 19956 | 2 sh | - 417 | $0 - 417 = 417$ | $A_0 - 3 \times 172$ |
| 19895 | 1 msh | - 478 | | $D_0 - 2 \times 172$ |
| 19850 | 1 msh | - 523 | | |
| 19824 | 1 msh | - 549 | $0 - 2 \times 279 = 558$ | |
| 19776 | 1 msh | - 597 | $0 - 597 = 597$ | $A_0 - 4 \times 172$ |
| 19706 | 1 sh | - 667 | | $B_0 - 4 \times 172$ |
| 19636 | 2 d | - 737 | $0 + 3 \times 30 - 837 = 747$ | $A_0 - 833$ |
| 19601 | 3 msh | - 772 | $0 + 2 \times 30 - 837 = 777$ | |
| 19566 | 5 msh | - 807 | $0 + 30 - 837 = 807$ | |
| 19536*** | 10 vsh | - 837 | $0 - 837 = 837$ | $B_0 - 833$ |
| 19458*** | 7 vsh | - 915 | $0 - 915 = 915$ | $A_0 - 833 - 172$ |
| 19409 | 3 sh | - 964 | $0 - 44 - 915 = 959$ | |
| 19372 | 5 vsh | - 1001 | $0 - 1001 = 1001$ | $B_0 - 833 - 172$ |
| 19346 | 2 d | - 1027 | $0 - 194 - 837 = 1031$ | |
| 19314 | 2 d | - 1059 | | |
| 19260 | 7 sh | - 1113 | $0 - 279 - 837 = 1116$ | $A_0 - 833 - 2 \times 172$ |
| 19219 | 2 msh | - 1144 | $0 - 44 - 279 - 837 = 1160$ | $B_0 - 833 - 2 \times 172$ |
| 19155 | 1 d | - 1218 | | |
| 19104 | 3 msh | - 1269 | $0 - 417 - 837 = 1254$ | $A_0 - 833 - 3 \times 172$ |
| 19063 | 2 msh | - 1310 | | $B_0 - 833 - 2 \times 172$ |
| 18936 | 2 msh | - 1437 | $0 - 597 - 837 = 1434$ | $A_0 - 833 - 4 \times 172$ |
| 18872 | 2 msh | - 1501 | | $B_0 - 833 - 4 \times 172$ |
| 18804 | 1 d | - 1569 | | |
| 18765 | 2 d | - 1608 | $0 + 2 \times 30 - 2 \times 837 = 1614$ | |
| 18732 | 5 msh | - 1641 | $0 + 30 - 2 \times 837 = 1644$ | |
| 18703*** | 10 vsh | - 1670 | $0 - 2 \times 837 = 1674$ | |
| 18626*** | 6 vsh | - 1747 | $0 - 915 - 837 = 1752$ | |
| 18587 | 1 d | - 1786 | $0 - 44 - 915 - 837 = 1796$ | |
| 18536 | 5 sh | - 1837 | $0 - 1001 - 837 = 1838$ | |
| 18483 | 1 d | - 1890 | $0 - 194 - 2 \times 837 = 1868$ | |
| 18431 | 4 sh | - 1942 | $0 - 279 - 2 \times 837 = 1953$ | |
| 18376 | 3 sh | - 1997 | $0 - 44 - 279 - 2 \times 837 = 1997$ | |

TABLE VI (contd.)

| Wave-number of the band cm ⁻¹ | Inten- sity | Shift from (0,0) band cm ⁻¹ | Assignment | |
|---|----------------|--|------------------------------|----------------|
| | | | Present author | Pant (1945) |
| (1) | (2) | (3) | (4) | (5) |
| 18299 | 2 d | -2074 | $0-417-2 \times 837=2091$ | |
| 18097 | 1 msh | -2276 | $0-795-2 \times 837=2271$ | |
| 18032 | 1 msh | -2341 | | |
| 17903 | 3 d | -2470 | $0+30-3 \times 837=2481$ | |
| 17875 | 8 sh | -2498 | $0-3 \times 837=2511$ | |
| 17797 | 5 sh | -2576 | $0-915-2 \times 837=2589$ | |
| 17744 | 1 d | -2629 | $0-44-915-2 \times 837=2633$ | |
| 17706 | 3 sh | -2667 | $0-1001-2 \times 837=2675$ | |
| 17646 | 1 d | -2727 | $0-194-3 \times 837=2705$ | |
| 17592 | 2 msh | -2781 | $0-279-3 \times 837=2790$ | |
| 17541 | 2 msh | -2832 | $0-44-279-3 \times 837=2834$ | |
| 17461 | 1 msh | -2912 | $0-417-3 \times 837=2928$ | |
| 17357 | 1 d | -3016 | | |
| 17184 | 1 d | -3189 | | |
| 17143 | 1 d | -3230 | | |
| 17055 | 2 msh | -3318 | $0+30-4 \times 837=3318$ | |
| 17024 | 5 sh | -3349 | $0-4 \times 837=3348$ | |
| 16951 | 3 sh | -3422 | $0-915-3 \times 837=3426$ | |
| 16851 | 2 sh | -3522 | $0-1001-3 \times 837=3512$ | |
| 16774 | 1 msh | -3599 | $0-279-4 \times 837=3627$ | |
| 16706 | 1 msh | -3667 | $0-44-279-4 \times 837=3671$ | |
| 16583 | 1 msh | -3790 | $0-417-4 \times 837=3675$ | |
| 16482 | 1 d | -3891 | | |
| 16202 | 2 sh | -4171 | $0-5 \times 837=4185$ | |
| 16134 | 1 sh | -4239 | $0-915-4 \times 837=4263$ | |
| 15326** | 1 vd | -5047 | $0-6 \times 837=5022$ | |

* These bands are also obtained in absorption.

** These bands are recorded at room temperature only.

*** These bands are obtained as emission bands in absorption experiments.

Uranyl chloride

The first strong band in fluorescence is at 20521 cm⁻¹ which is also strong in absorption (value 20530 cm⁻¹). Therefore, this band is chosen as the (0, 0) band. The other bands could be interpreted on the basis of three fundamentals in the ground state 880 cm⁻¹ (symmetric stretching), 964 cm⁻¹ (asymmetric stretch-

ing) and 246 cm^{-1} (symmetric bending) and one fundamental in the upper state 26 cm^{-1} (crystal lattice frequency) (Table V). It is seen that the 880 fundamental and its overtones are weaker in intensity than 964 fundamental and its combinations with 880 fundamental fig. 5, Plate V (A) which shows violation of selection rules due to the crystalline fields.

Potassium uranyl sulphate

The first strong band at 20373 cm^{-1} is chosen as the $(0, 0)$ band for reasons similar to those in acetate. Most of the other bands could be explained on the basis of five fundamentals in the ground state 837 cm^{-1} (symmetric stretching), 915 cm^{-1} (asymmetric stretching), 194 and 279 cm^{-1} (symmetric bending) and 44 cm^{-1} (crystal lattice frequency) and two fundamentals in the upper state 662 cm^{-1} (symmetric stretching) and 30 cm^{-1} (crystal lattice frequency) (Table VI). Among the two fundamentals belonging to the bending vibration, 194 cm^{-1} corresponds to the in-plane bending frequency and 279 cm^{-1} corresponds to the out-of-plane bending frequency of the uranyl ion. These two frequencies arise due to the removal of degeneracy in the linear $\text{O}-\text{U}-\text{O}$ ion which becomes slightly bent in the crystalline fields. The out-of-plane bending fundamental is stronger than the in-plane bending fundamental. As in sulphate, in the case of potassium uranyl sulphate also, the bands analysed as $0-279-n \times 837$ appear with moderately strong intensity which shows the importance of the bending frequency. This may be taken as an indication that the uranyl ion is slightly more bent than in acetate, nitrate, etc. Sevchenko and Stepanov (1949) who studied the infra red absorption of this substance have come to the conclusion that the ion is slightly bent as some bands forbidden for a linear model of the uranyl ion are present in the spectrum.

Three possible fundamentals 417 , 597 , and 1001 cm^{-1} of the sulphate ion have been used in the analysis to explain some of the weak bands. These frequency values agree well with the Raman values given for the sulphate ion in sulphuric acid (Hibben, 1939).

Ammonium uranyl sulphate

The first strong band at 20348 cm^{-1} has been chosen as the $(0, 0)$ band for the same reasons as in acetate etc. About 45 bands have been analysed on the basis of the five fundamentals in the ground state 848 cm^{-1} (symmetric stretching), 926 (asymmetric stretching), 207 cm^{-1} (in-plane bending) frequency, 273 cm^{-1} (out-of-plane bending frequency) and 29 cm^{-1} (crystal lattice frequency) and two fundamentals in the upper state 697 and 24 cm^{-1} (Table VII). As in the case of potassium uranyl sulphate, the two frequencies 207 and 273 cm^{-1} arise due to the removal of degeneracy in the linear $\text{O}-\text{U}-\text{O}$ ion, which becomes slightly bent in the crystal line fields. Three possible fundamentals 473 , 626 , and 1195 cm^{-1}

TABLE VII

Fluorescence bands of ammonium uranyl sulphate

| Wave-number of the band cm ⁻¹ | Inten- sity | Shift from (0,0) band cm ⁻¹ | Assignment |
|---|----------------|--|--------------------|
| (1) | (2) | (3) | (4) |
| 21045* | 1 vd | + 697 | 0+697=697 |
| 20410** | 1 d | + 62 | 0+2×24=48 |
| 20372 | 3 d | + 24 | 0+24=24 |
| 20348** | 7 sh | | (0,0) |
| 20319 | 4 d | - 29 | 0-29=29 |
| 20248 | 4 d | - 100 | |
| 20171 | 1 d | - 177 | 0+24-207=183 |
| 20141 | 2 msh | - 207 | 0-207=207 |
| 20075 | 3 sh | - 273 | 0-273=273 |
| 19995 | 1 msh | - 353 | |
| 19931 | 1 msh | - 417 | 0-2×207=414 |
| 19875 | 2 sh | - 473 | 0-473=473 |
| 19722 | 1 sh | - 626 | 0-626=626 |
| 19695 | 1 d | - 653 | 0-29-626=655 |
| 19563 | 2 d | - 785 | 0+2×24-484=800 |
| 19529 | 4 d | - 819 | 0+24-848=824 |
| 19500*** | 10 sh | - 848 | 0-848=848 |
| 19422*** | 8 sh | - 926 | 0-926=926 |
| 19311 | 4 d | -1037 | 0-207-848=1055 |
| 19225 | 4 d | -1123 | 0-278-848=1121 |
| 19153 | 2 msh | -1195 | 0-1195=1195 |
| 19092 | 1 msh | -1256 | 0-2×207-848=1262 |
| 19031 | 3 sh | -1317 | 0-473-848=1321 |
| 18967 | 1 msh | -1381 | |
| 18878 | 2 sh | -1470 | 0-626-848=1474 |
| 18718 | 1 d | -1630 | 0+2×24-848=1648 |
| 18687 | 2 d | -1661 | 0+24-2×848=1672 |
| 18666*** | 10 sh | -1682 | 0-2×848=1696 |
| 18583*** | 8 sh | -1765 | 0-926-848=1774 |
| 18468 | 4 d | -1880 | 0-207-2×848=1903 |
| 18378 | 4 d | -1970 | 0-273-2×848=1969 |
| 18307 | 1 d | -2041 | 0-1195-848=2043 |
| 18187 | 2 sh | -2162 | 0-473-2×848=2169 |
| 18120 | 1 msh | -2228 | |
| 18036 | 2 sh | -2312 | 0-626-2×848=2322 |
| 17842 | 1 d | -2506 | |
| 17830 | 8 sh | -2518 | 0-3×848=2544 |
| 17750 | 6 sh | -2598 | 0-926-2×848=2622 |
| 17642 | 3 d | -2706 | 0-207-3×848=2751 |
| 17537 | 3 d | -2811 | 0-273-3×848=2817 |
| 17556 | 2 msh | -2891 | 0-1195-2×848=2891 |
| 17378 | 1 msh | -2970 | 0-2×207-3×848=2958 |
| 17361 | 1 d | -2987 | 0-473-3×848=3017 |
| 17192 | 1 d | -3156 | 0-726-3×848=3170 |

TABLE VII (contd.)

| Wave-number of the band cm^{-1} | Intensity | Shift from (0,0) band cm^{-1} | Assignment |
|--|-----------|--|-----------------------------|
| (1) | (2) | (3) | (4) |
| 16959 | 6 sh | -3389 | $0-4 \times 848 = 3392$ |
| 16878 | 4 sh | -3470 | $0-926-3 \times 848 = 3470$ |
| 16791 | 2 sh | -3557 | $0-207-4 \times 848 = 3599$ |
| 16686 | 1 msh | -3662 | $0-273-4 \times 848 = 3655$ |
| 16147 | 2 sh | -4201 | $0-5 \times 848 = 4240$ |
| 16073 | 2 sh | -4275 | $0-926-4 \times 848 = 4318$ |
| 16016 | 1 d | -4332 | |

* This band is recorded at room temperature only.

** These bands are obtained in absorption also.

*** These bands are obtained as emission bands in absorption experiments.

of the sulphate ion are also identified and used in the analysis to explain some weak bands in between the groups. These frequency values are found to agree well with the Raman values given for the sulphate ion in sulphuric acid (Hibben, 1939).

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A GENERAL TREATMENT OF PENETRATION FACTOR IN ALPHA-DECAY

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ABSTRACT. A general treatment of the calculation of the penetration probability of alpha-particles through a potential barrier of Woods-Saxon diffuse type nuclear potential along with the Coulomb potential has been given according to the one-body model for arbitrary values of the angular momentum of the emitted alpha-particles. In the region where practically only the Coulomb potential is present the rigorous solution of Schrödinger equation has been taken from that of Abramowitz. Near the nuclear boundary where both the potentials operate, the Schrödinger equation has been solved by an ingenious method due to Lanczos.

INTRODUCTION

Uptil now, the calculation of the penetration factor in alpha-decay has mostly been based on the WKB method. But it does not seem justified to put much reliance on the results derived by this method without proper investigation specially when the validity of that method has been doubted at times (Blatt and Weisskopf, 1954). So this problem has been tried by a method due to Lanczos (1938). In doing so, the one-body model was followed and for the nuclear potential use was made of the Woods-Saxon diffuse potential which drops exponentially beyond the nuclear surface, besides that the Coulomb potential is present throughout the region. In the region where the Coulomb field predominates the Schrödinger equation has been solved by the Riccati-I method as treated by Abramowitz (1949) (c.f. Froberg, 1955). The Schrödinger equation in the neighbourhood of the nuclear boundary has been solved by the method of Lanczos (1938).

In a previous publication by Dutta, Mitra and Sil (1960), hereafter referred to as I, a calculation of the penetration factor in the process of alpha-decay following one body model has been given for the case of $l = 0$, where the potential field was the same as in this case. In I, for the sake of simplification the Coulomb potential was taken to be constant near the nuclear surface. In the present paper that simplification has been dispensed with and the equation takes into account any arbitrary values of l . Consequently the method of solution for this general case has been different from that of I.

In the method given in I, the differential equation was equated instead of to zero, to an error term proportional to the Tshebysheff's polynomial of a given order. As a result a finite power series solution was obtained, the coefficients of which were easily calculated with the help of a set of recursion relations. In that case the error term vanished at the zero points of the Tshebysheff's polynomial and the error involved in the solution was at the most 1 in 10^8 .

In the present case, the differential equation contains the Woods-Saxon exponential term, the Coulomb $\frac{1}{r}$ term and the centrifugal $\frac{l(l+1)}{r^2}$ term and the method of solution, though different from that in I, has also been given by Lanczos (1938). The approximate solution of such a general differential equation which can not be equated to any polynomial, is obtained in the form of a finite power series solution. The coefficients of the power series are evaluated by demanding the vanishing of the differential equation at the zero points of the Tshebysheff's polynomial and thus by solving a set of simultaneous linear equations.

The method given here is a generalisation of the method given in I, to include the cases of differential equation with non-rational coefficients; for the differential equation with rational coefficients this method yields exactly the same coefficients obtained by the method given in I.

The penetration factor has been calculated from the value of the wave function at the point near the nuclear boundary where the potential energy is equal to the kinetic energy of the emitted alpha-particle.

On comparing our results with those obtained by the WKB method it appears that both the sets agree well with each other.

MATHEMATICAL FORMULATION

The equation for u , which is r times the wave function of the radial part of the Schrödinger equation can be written as

$$\frac{d^2u}{dr^2} + \frac{2m}{\hbar^2} \left[E - U(r) - V(r) \right] u = 0, \quad \dots (1)$$

where
$$U(r) = \frac{2(Z-2)e^2}{r} + \frac{\hbar^2}{2m} \cdot \frac{l(l+1)}{r^2}$$

and
$$V(r) = \frac{-V_0}{1 + e^{(r-R)/a}}$$

For convenience of calculation, we neglect $V(r)$ beyond the point r_1 where the nuclear potential drops to $\frac{-V_0}{100}$.

To solve Eq. (1) the space is divided into two regions $r_2 \leq r \leq r_1$ and $r > r_1$, r_2 being the point where the potential energy is equal to the kinetic energy of the emitted α -particle. In the latter region only the Coulomb potential is of any value.

To solve Eq. (1) in the region $r_2 \leq r \leq r_1$ Eq. (1) is rewritten by changing the independent variable to $x = r/a$, as follows :

$$\frac{d^2u}{dx^2} + \left[\frac{\lambda^2}{1+\beta e^x} - f(x) - K^2 \right] u = 0, \quad \dots (2)$$

where $\lambda^2 = \frac{2ma^2}{\hbar^2} V_0$, $\beta = e^{-R/a}$, $K^2 = \frac{2ma^2}{\hbar^2} \{U(ax_1) - E\}$

and $f(x) = \frac{2ma^2}{\hbar^2} [U(ax) - U(ax_1)]$.

$U(ax)$ and $U(ax_1)$ being the values of $U(r)$ and $U(r_1)$ respectively on changing the independent variable.

Let us suppose the solution to be of the form,

$$u \sim e^{\mp Kx} \cdot F_{\mp}$$

Thus the Eq. (2) becomes

$$\frac{d^2F_{\mp}}{dx^2} \mp 2K \frac{dF_{\mp}}{dx} + \left\{ \frac{\lambda^2}{1+\beta e^x} - f(x) \right\} F_{\mp} = 0 \quad \dots (3)$$

Again, substituting $z = e^{-x}$ and putting $\frac{z+\beta}{z} f(x) = \phi(z)$, the Eq. (3) becomes

$$z(z+\beta) \frac{d^2F_{\mp}}{dz^2} + (z+\beta)(1 \pm 2K) \frac{dF_{\mp}}{dz} + \{\lambda^2 - \phi(z)\} F_{\mp} = 0 \quad \dots (4)$$

For later calculations the independent variable occurring as the argument of the Tshebysheff's polynomial has to be normalised such that it varies from zero to one; so we make the transformation

$$p = \frac{z-z_1}{z_2-z_1}.$$

Thus we get from Eq. (4)

$$(p+\mu)(p+\nu) \frac{d^2F_{\mp}}{dp^2} + \delta(p+\nu) \frac{dF_{\mp}}{dp} + \{\lambda^2 - \chi(p)\} F_{\mp} = 0, \quad \dots (5)$$

where $\mu = \frac{z_1}{z_2 - z_1}$, $\nu = \frac{z_1 + \beta}{z_2 - z_1}$, $\delta = 1 \pm 2k$, $\chi(p) = \phi(z)$.

For F , a certain polynomial of n th order in p has been assumed which satisfy the above differential equation at the zeros of the Tshebysheff's polynomial of order n .

Let $F = \sum_{i=0}^n a_i p^i$, where $a_0 = 1$.

and p_1, p_2, \dots, p_n are the roots of the equation

$$T_n(p) = 0,$$

where $T_n(p)$ is the Tshebysheff's polynomial of order n . Then on substitution of the polynomial $\sum_{i=0}^n a_i p^i$ for F in the Eq. (5) we have a set of n simultaneous equations :

$$(p_i + \mu)(p_i + \nu) \left(\frac{d^2 F}{dp^2} \right)_{p_i} + \delta(p_i + \nu) \left(\frac{dF}{dp} \right)_{p_i} + \{\lambda^2 - \chi(p_i)\} F = 0, \quad \dots (6)$$

which may be written after rearrangement as

$$a_1 f_1(p_i) + a_2 f_2(p_i) + a_3 f_3(p_i) + \dots + a_n f_n(p_i) = g(p_i),$$

f_r 's and g are known functions of p and are given by

$$f_r(p_i) = r(r-1)p_i^{r-2}(p_i + \mu)(p_i + \nu) + r p_i^{r-1} \delta(p_i + \nu) + p_i^r \{\lambda^2 - \chi(p_i)\}$$

and

$$g(p_i) = -\{\lambda^2 - \chi(p_i)\}.$$

This set of n simultaneous linear equations can be written as

$$\begin{pmatrix} f_{11} & f_{21} & f_{31} & \dots & f_{n1} \\ f_{12} & f_{22} & f_{32} & \dots & f_{n2} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ f_{1n} & f_{2n} & f_{3n} & \dots & f_{nn} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \cdot \\ \cdot \\ \cdot \\ a_n \end{pmatrix} = \begin{pmatrix} g_1 \\ g_2 \\ \cdot \\ \cdot \\ \cdot \\ g_n \end{pmatrix}$$

where

$$f_{jk} = f_j(p_k)$$

and

$$g_k = g(p_k).$$

From the above the values of the coefficients of the power series are determined. Therefore the solution of the differential equation is known except for an arbitrary

constant multiplier. The two values of δ give two solutions $F_+(p)$ and $F_-(p)$ corresponding to negative and positive value of δ . Therefore, the solution near the surface of the nucleus ($r_2 < r < r_1$) is

$$u = Ae^{-kx} F_-(p) + Be^{+Kx} F_+(p). \quad \dots (7)$$

Now, in the region ($r > r_1$) only Coulomb potential is effective and the Schrödinger equation takes the form

$$\frac{d^2u}{d\rho^2} + \left\{ 1 - \frac{2\eta}{\rho} - \frac{l(l+1)}{\rho^2} \right\} u = 0, \quad \dots (8)$$

where $\rho = \alpha \cdot r = \sqrt{\frac{2mE}{\hbar^2}} \cdot r, \quad 2\eta = \frac{2m}{\hbar^2} \cdot \frac{2(Z-2)e^2}{\alpha}.$

The Eq. (8) has two solutions: $F_l(\eta, \rho)$ regular at the origin and $G_l(\eta, \rho)$ irregular at the origin, and are defined by their asymptotic behaviour:

$$F_l(\eta, \rho) \sim \sin \theta_l,$$

$$G_l(\eta, \rho) \sim \cos \theta_l,$$

when $\rho \rightarrow \infty.$

where $\theta_l = \rho - \eta \log 2\rho - \frac{l}{2}\pi + \sigma_l$ and $\sigma_l = \arg \Gamma(i\eta + l + 1).$

The boundary condition that at infinity the alpha-particle should behave as a free out-going particle is satisfied by the linear combination $G_l + iF_l$, which represents a pure out-going wave.

When l is an integer, F_{l+1} (or G_{l+1}) can be computed with the help of a set of recurrence relations given by Powell (1947) provided F_l (or G_l) and its first derivative F'_l (or G'_l) are known. If y_l stands for either $F_l(\eta, \rho)$ or $G_l(\eta, \rho)$ the recurrence relations satisfied by it are:

$$(l+1) \frac{dy_l}{d\rho} = \left[\frac{(l+1)^2}{\rho} + \eta \right] y_l - [(l+1)^2 + \eta^2]^{\frac{1}{2}} y_{l+1}, \quad \dots (9)$$

$$l[(l+1)^2 + \eta^2]^{\frac{1}{2}} y_{l+1} = (2l+1) \left[\eta + \frac{l(l+1)}{\rho} \right] y_l - (l+1)[l^2 + \eta^2]^{\frac{1}{2}} y_{l-1}, \quad (10)$$

$$l \frac{dy_l}{d\rho} = (l^2 + \eta^2)^{\frac{1}{2}} y_{l-1} - \left(\frac{l^2}{\rho} + \eta \right) y_l, \quad \dots (11)$$

If the values of F_0 (or G_0) and F'_0 (or G'_0) are known by the application of Eq. (9) F_1 (or G_1) can be computed and subsequently by the application of Eq. (10) the values of F_l (or G_l) for higher values of l can be obtained. The values of F'_l (or G'_l) are computed with the help of Eq. (11).

Now F_0 and G_0 have different representations in the different ranges defined by the values of ρ and η . In the range where $\rho < 2\eta$, which is the case here,

the representations of F_0 and G_0 are given by Abramowitz, based on Riccati's method as quoted by C. G. Froberg (1955).

$$F_0 = \frac{1}{2}e^{\Phi(t, \eta)} \quad G_0 = e^{\bar{\Psi}(t, \eta)}, \quad \text{where } t = \frac{\rho}{2\eta}.$$

$$\Phi(t, \eta) = 2\eta g_0 + g_1 + (2\eta)^{-1}g_2 + (2\eta)^{-2}g_3 + \dots$$

$$\bar{\Psi}(t, \eta) = -2\eta g_0 + g_1 - (2\eta)^{-1}g_2 + (2\eta)^{-2}g_3 - \dots$$

where $g_0, g_1, g_2 \dots$ etc are given functions of t .

The values of the constants A and B in Eq. (7) are found with the help of the continuity condition of u and du/dr at the point $r = r_1$. The values of F_l and dF_l/dr are found to be negligible in comparison with that of G_l and dG_l/dr at that point. Next, the value of u at $r = r_2$ is calculated from the Eq. (7), from which the penetration factor is determined by following the definition of Blatt and Weisskopf (1954),

$$P = \frac{1}{|u(r_2)|^2}.$$

$u(r_2)$ is given by the following expression :

$$u(r_2) = Ae^{-K^{22}} F_-(1) + Be^{+K^{22}} F_+(1)$$

since at $r = r_2$, $p = 1$.

We may write the disintegration constant as

$$\lambda = N.P,$$

where N is the number of times the α -particle hits the barrier wall. If the α -particle moves with a velocity v within the crater of the nucleus of radius R , then $N = v/2R$. We determine v from the condition that the motion of the α -particle within the nucleus of radius R is such that the associated waves form nodes at $r = R$.

If $x_{l,k}$ is the $(k+1)$ th root ($kR = 0$, being the first root) of the equation $J_{l+\frac{1}{2}}(kR) = 0$,

$$\text{then} \quad N = \frac{\hbar}{4mR^2} \cdot \frac{x_{l,k}}{\pi}.$$

Now the half-life can be calculated from the expression

$$T = \frac{\log_e 2}{\lambda}$$

where

$$\lambda = \frac{\hbar \cdot P}{4mR^2} \cdot \frac{x_{l,k}}{\pi}$$

TABLE I

| Ele- ment | A mass no. | Z charge no. | R in fermi nuclear radius | m in gm. the reduced mass of the α - particle | l | r_2 in fermi where P.E. energy = $K.E.$, with of the screening α - particle correc- tion | E in Mev. the α - particle | $F_-(l)$ | $F_+(l)$ | P calculated by WKB method | T in sec. value of half-life | |
|--------------|------------------|--------------------|---------------------------------------|--|---|---|--|-----------|----------|-------------------------------------|---------------------------------------|--------------------------|
| Rn | 218 | 86 | 9.3749 | 6.5223×10^{-24} | 0 | 9.5726 | 7.162 | + .78267 | -1.2319 | 3.555×10^{-10} | 4.67×10^{-10} | $.6747 \times 10^{-2}$ |
| | | | | | 2 | 9.5230 | 6.564 | + .76893 | -1.9406 | 1.220×10^{-21} | 1.62×10^{-21} | 107.16×10^{-2} |
| Th | 230 | 90 | 9.5231 | 6.5286×10^{-24} | 0 | 9.5538 | 4.718 | + .72373 | -4.54306 | 4.937×10^{-33} | 6.61×10^{-33} | $.5019 \times 10^{12}$ |
| | | | | | 3 | 9.50198 | 4.404 | + .71005 | -6.32904 | $.7447 \times 10^{-35}$ | 1.04×10^{-35} | 149.456×10^{12} |
| Pu | 238 | 94 | 9.6190 | 6.5325×10^{-24} | 0 | 9.64396 | 5.535 | + .725805 | -4.7648 | 7.543×10^{-39} | 9.30×10^{-39} | $.335 \times 10^{19}$ |
| | | | | | 4 | 9.5777 | 5.394 | + .711196 | -7.13057 | 1.911×10^{-41} | 2.45×10^{-41} | 4.994×10^{19} |

TABLE II

| Ele- ment | A | Z | l | E in MeV. | m in gm. | Value of P by the method of calculation | | | Value of T calculated from that of P obtained by using the method | | Expt. value of T in sec. |
|--------------|-----|----|---|--------------|------------------------|--|------------------------------|---------------------------|---|-----------------------------------|--------------------------------|
| | | | | | | As given in I | As given in this paper | P by WKB method | given in I in sec. | given in this paper in sec. | |
| Po | 214 | 84 | 0 | 7.714 | 6.52×10^{-24} | 1.337 $\times 10^{-10}$ | 1.179 $\times 10^{-10}$ | 1.58 $\times 10^{-10}$ | .177 $\times 10^{-4}$ | .2012 $\times 10^{-4}$ | 1.636×10^{-4} |

RESULTS

The numerical calculations have been done for the following elements, for different values of l , to show the applicability of the method. The values of parameters are the same as used by Igo and Thaler (1957).

$$R = 1.35A^{1/3} + 1.3 \text{ fermi, } a = 0.5 \text{ fermi, } V_0 = 45 \text{ Mev.}$$

In our calculation we have taken $n = 4$ and $k = 1$. Results are shown in Table I.

The values of half-life as calculated here, are lower than the experimental values of the same for the case $l = 0$ only, whereas for $l = 2, 3$, or 4 they are all greater than the experimental values. The values of the penetration factor calculated by the method given here appear to be consistently lower than that calculated by the WKB method for all values of l . The values of P by WKB method and the experimental value of half-life and that of E are taken from the table given by Rassmussen (1959) in his paper on the penetration probability of alpha-particles.

It may be worth while to compare the results for the case $l = 0$ as obtained here with that of the previous method where the Coulomb potential near the nuclear boundary was taken to be of constant value. In our present case, as expected, the value of P is slightly lower than that obtained by the previous method. The differences in the figures given in Table II indicate the measure of error involved in the approximation about the Coulomb potential in the previous method.

In the paper I, due to some numerical slip in the value of a parameter, the penetration factor of $^{214}\text{Po}_{84}$ for $l = 0$ was found to be $.059 \times 10^{-16}$ which should, instead, be 1.3373×10^{-16} .

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INTENSITY MEASUREMENTS IN MOLECULAR BANDS

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ABSTRACT. Peak and integrated intensities of N_2 II positive bands have been measured. The peak values have been corrected according to the procedure of Floyd and King. The data have been obtained with a view to assess the reliability of peak intensity measurements and also the correction due to Floyd and King.

Intensity of a band to be accurate has to be obtained by summing over the intensities of the rotational lines that form the band. Phillips (1957) tried to use this principle for the C_2 (Swan) system excited in a furnace of known temperature. Since the lines were badly blended he calculated band profiles by combining the profiles of individual rotational lines. He concludes that the results so obtained may be quite uncertain for weak bands. However, a rigorous application of the method is too laborious and many times it is not practicable or even possible. So simpler, but reliable, methods of estimating intensity are to be thought of. The method—known as integrated intensity method—of measuring intensities with a low dispersion spectrograph by integrating over the entire intensity contour of the bands is the one which gives intensity values nearest to the true intensity of a band. The requirements for the results to be reliable are (i) the band structure should not be resolved and (ii) there should be no overlapping from the neighbouring bands. The first requirement can be easily met by a proper choice of the spectrograph, but the second requirement is too rarely satisfied, because in almost all actual band systems there is an overlapping from neighbouring bands. When the overlapping is present, the band profiles are judiciously extrapolated and the effect of overlapping separated. But such a procedure is purely subjective and the results might be in great error for weaker bands overlapped by strong bands.

In case of overlapping, the intensity at the head of the band may be taken to represent band intensity (peak intensity method) or a known fraction of band intensity near head may be used to derive band intensity (fractional band intensity method, Robinson and Nicholls, 1958).

Ornstein and Brinkman (1931) were the earliest to use the peak intensity of CN bands to represent band intensity and concluded that the rotational energy distribution varies from band to band and hence the method is not valid. Tawde and Patankar (1943) have shown for N_2 second positive system that the ratio of

the band head intensity to integrated intensity is not a constant, while Young (1954) has shown experimentally for the same system that the mean deviation for this ratio is only 6.2%.

Floyd and King (1955) have developed a method of obtaining total band intensity from the band head intensity, by assigning a representative rotational quantum number for the band head (J_h) and also taking into account the number of lines forming the head (ΔJ). This method finds immediate application to singlet systems or for those systems which can be approximated to singlet systems. A difficulty in applying the method is that the temperature of the source (emitting the band system) which enters into the equation is, in general, not precisely known. For many sources true temperatures are not easily available or estimable. So the method might not find rigorous application to all the band systems. However, a fairly satisfactory intensity value may be obtained, if we can assume some reasonable temperature or approximate the term containing temperature to a constant. This can be done provided the rotational quantum number at the band head has a small range of variation in the bands considered.

Robinson and Nicholls (1958) have developed a fractional band intensity method which correlates the sum of intensities of a few rotational lines at and near the head with the band intensity. This method also suffers from lack of knowledge of temperature which has therefore to be assumed.

A possible error in peak intensity and fractional band intensity measurements is the effect of self-absorption on the intensity at the peak. This effect becomes appreciable when the intensity of the blended rotational lines reaches a significant fraction of the intensity of a black body at the same temperature and wavelength. In that case one will have to consider the manner of blending of rotational lines at the band head.

Robinson and Nicholls (1958) have developed a rotational line intensity method, where the intensities of rotational lines are plotted against the energy of upper levels of transition. The intercept on this graph can be used to obtain band intensity. The method is satisfactory provided rotational thermodynamic equilibrium exists in the source.

Intensities of $\text{NO}(\beta)$ and O_2 (II negative) systems were measured by these methods by the above authors and the results were found to compare satisfactorily with the integrated intensity values. But it may be noted here that the integrated intensity values are subject to the error due to overlapping by the neighbouring bands.

In order to judge the merits and demerits of any method for intensity measurements, it is necessary to possess integrated intensity values on bands which have no appreciable overlapping. So it was decided to measure the intensities of bands N_2 (II positive) system with a view to ascertain the reliability of peak intensities and peak intensities corrected according to the method of Floyd

and King (1955). The reason for selecting only these two is that such values are easily available and an evaluation of their reliability is naturally much useful. The bands (1-6), (2-7), (3-8), (1-5), (2-6) and (3-7) have almost negligible overlapping from neighbouring bands and hence they have been particularly chosen for this study. The intensities have been measured photographically using an a.c. discharge through air as a source of N_2 (II positive) bands. The measurements have been repeated with two spectrographs to ascertain the effect of varying dispersion on the intensity measurements and also as a general check on the measurements.

TABLE I
Intensity measurements— N_2 II P. (small quartz spectrograph)

| Transi- tion | $*I_p$ | $*I_{pc}$ | $*I$ | $\frac{I_p}{I}$ | Devn. from mean | $\frac{I_{pc}}{I}$ | Devn. from mean |
|-----------------|--------|-----------|--------|-----------------|-----------------------|--------------------|-----------------------|
| 1-6 | 25.36 | 26.92 | 30.61 | 0.83 | 0.09 | 0.88 | 0.07 |
| 2-7 | 32.64 | 34.93 | 38.13 | 0.86 | 0.06 | 0.92 | 0.03 |
| 3-8 | 28.69 | 31.19 | 32.89 | 0.87 | 0.05 | 0.95 | 0.00 |
| 1-5 | 93.94 | 92.11 | 95.34 | 0.99 | 0.07 | 0.97 | 0.02 |
| 2-6 | 100.00 | 100.00 | 100.00 | 1.00 | 0.08 | 1.00 | 0.05 |
| 3-7 | 65.01 | 65.72 | 66.24 | 0.98 | 0.06 | 0.99 | 0.04 |

Mean 0.92 Mean 0.95
Mean % devn.: 7.5 Mean % devn.: 4.2

TABLE II
Intensity measurements— N_2 II P. (medium quartz spectrograph)

| Transi- tion | $*I_p$ | $*I_{pc}$ | $*I$ | $\frac{I_p}{I}$ | Devn. from mean | $\frac{I_{pc}}{I}$ | Devn. from mean |
|-----------------|--------|-----------|--------|-----------------|-----------------------|--------------------|-----------------------|
| 1-6 | 20.43 | 21.39 | 19.09 | 1.07 | 0.07 | 1.12 | 0.09 |
| 2-7 | 23.27 | 24.65 | 22.53 | 1.03 | 0.03 | 1.09 | 0.05 |
| 3-8 | 21.16 | 22.78 | 21.89 | 0.97 | 0.03 | 1.04 | 0.00 |
| 1-5 | 99.98 | 98.14 | 98.16 | 1.02 | 0.02 | 1.00 | 0.04 |
| 2-6 | 100.00 | 100.00 | 100.00 | 1.00 | 0.00 | 1.00 | 0.04 |
| 3-7 | 70.20 | 71.58 | 74.83 | 0.94 | 0.06 | 0.96 | 0.08 |

Mean 1 Mean 1.04
Mean % devn.: 5 Mean % devn.: 5

- * I_p Peak intensity,
 I Integrated intensity, and
 I_{pc} Peak intensity corrected according to Floyd and King (see Appendix).

The results are collected in Tables I and II. It is observed that the percentage mean deviation is not more than 7% in the case of uncorrected peaks and not more than 5% in the case of corrected peaks. Considering the fact that photographic photometry has errors of these magnitude, we feel that the peak values compare fairly well with integrated values; and corrected peak values, in general, give a better comparison with integrated values. In connection with corrected values, it may be noted that the exponential term containing the rotational temperature has been approximated to a constant. However, if a temperature, say 300°C, is assumed for the discharge, the change in value of intensities is $\sim 2\%$ and hence the approximation of the term might be justified.

APPENDIX

$$I_{pc} = I_p \left[J_h \Delta J \right]^{-1} \exp \left[\frac{B_{v'} J_h (J_h - 1)}{kT} \right]$$

where J_h the rotational quantum number at band head, is expressed as

$$J_h = \frac{B_{v'} + B_{v''}}{2(B_{v'} - B_{v''})}$$

and ΔJ the number of lines forming band head is given by

$$= \frac{\text{Const}}{\lambda_h} \left[\frac{d\lambda}{ds} / (B_{v'} - B_{v''}) \right]^{\frac{1}{2}}$$

where λ_h = wavelength at band head.

The symbols in the above have their usual meaning (Herzberg, 1950).

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ON THE SUPERHEAT OF LIQUIDS

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ABSTRACT. A new method for measuring maximum superheat temperatures of liquids has been devised. A thin-walled degassed pyrex glass bulb, set vibration free and dipped in liquid, was heated by a coil immersed in mercury filling the bulb. This heating surface was chosen because it introduced minimum heterogeneity at the liquid-solid interface. The temperature of the liquid bulk was kept close to the boiling point using a paraffin oil bath. The temperature of the heater surface was increased in regular steps and the temperature at which the boundary film of the liquid exploded with vigorous ebullition was taken as the maximum superheat temperature of the liquid. Results obtained with carbon tetrachloride, chloroform, acetone, benzene, methyl alcohol, carbon disulphide, diethyl ether, *n*-pentane and ethyl bromide have been compared with the values obtained by Kenrick, Gilbert and Wismer (1924) as well as with those deduced from Van der Waals equation. The agreement is fair.

The set-up seems to offer a practical method for studying the effect of varying the nature of the interface on the superheat of liquids.

INTRODUCTION

The study of superheat of liquids is important for investigating the theoretical basis of homogeneous nucleation and also from the standpoint of defining the heterogeneity in a two-phase heating system. The latter has received a great impetus in recent years with the introduction of the bubble chamber as a means of detecting charged particles.

Many different methods have been used to investigate the maximum degree of superheat attainable in liquids at atmospheric pressure. Wismer *et al.* (1924) adopted the method of superheating liquids in capillaries, Briggs (1951, 1955) carried out his tests using a centrifuge, while Harvey *et al.* (1947) used the pressure pulse method; in both the latter cases the liquids tended to cavitate under negative pressure. The work of Wakeshima and Takata (1958) in this field is more recent. In their device droplets of liquids were introduced into a vertical column of an immiscible liquid possessing a steady temperature gradient in order to find at which temperature-level the liquid drop exploded during its ascent.

These methods have the common purpose of reaching the theoretical maximum superheat temperature. They are hardly applicable to constant flow or steady transfer systems in which a thin layer in contact with the heater surface becomes strongly heated whilst the bulk of the liquid remains at a temperature near the boiling point.

The principle of the present work is based on a model of practical heat transfer systems. Here a thin-walled pyrex glass bulb filled with mercury is chosen as the heating surface. The bulb is degassed and dipped into the liquid to be studied. The mercury in the bulb is heated electrically by a coil and the temperature of the liquid bulk is kept very close to its boiling point by regulating its temperature with the help of a jacketing paraffin oil bath. In the steady heat flow condition the temperature of the stagnant film of the liquid in contact with the outer surface of the glass bulb naturally attains a steady high value ; just beyond it the temperature falls sharply. As the heat input of the coil is increased in steps and sufficient time is allowed for the system to acquire steady-state for each step, the boundary liquid film becomes increasingly superheated in the successive steps until it ruptures with explosion, giving rise to vigorous ebullition from innumerable centres on the bulb surface simultaneously. The highest steady state surface temperature of the bulb is taken to be the maximum superheat temperature of the liquid and this is calculated from the steady temperature of the mercury after correcting for the temperature drop across the glass wall of the bulb.

The results obtained with different organic liquids agree fairly well with

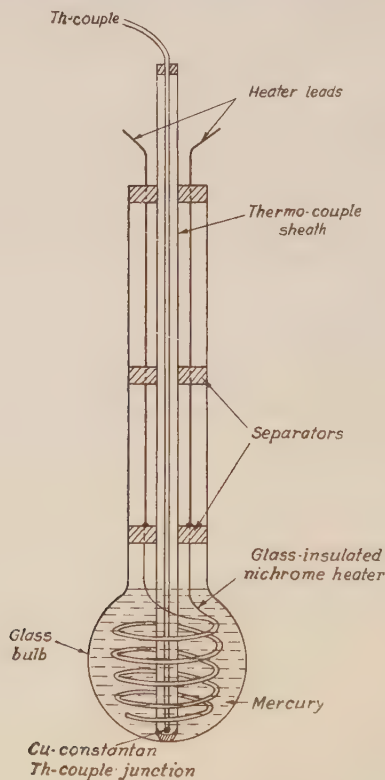


Fig. 1. Glass-bulb heater assembly.

those of Wismer *et al.* (1924) and also with the theoretical values calculated from Temperley's (1947) adaptation of the Van der Waals equation.

EXPERIMENTAL APPARATUS

The experimental set up consists of (1) glass bulb heater assembly, (2) degassing flask, and (3) the temperature regulating bath.

1. A schematic diagram of the glass bulb heater assembly is given in Fig. 1. A pyrex brand glass tube of 0.76 cm. bore and 30 cm. in length was taken and a spherical bulb of 2.1 cm. diameter with a fairly uniform wall thickness of 0.05 cm. was blown at one end. The bulb was filled with mercury. A glass insulated nichrome wire (33 swg) heater coil was immersed in the mercury. In positioning the coil care was taken to ensure that it did not touch the inner surface of the glass bulb. The electrical input to the heating coil was taken from 220 volts D.C. mains and it was closely regulated and controlled by a bank of rheostats so that the temperature of the mercury could be increased very slowly. Temperature of the mercury was measured by a copper-constantan thermocouple, contained in a thin-walled glass sheath, the reference junction being at the ice point. The thermocouple was calibrated after insertion in the glass bulb. The thermocouple voltage was measured by a Diesselhorst Potentiometer.

2. The provisions for degassing the bulb is shown in Fig. 2.

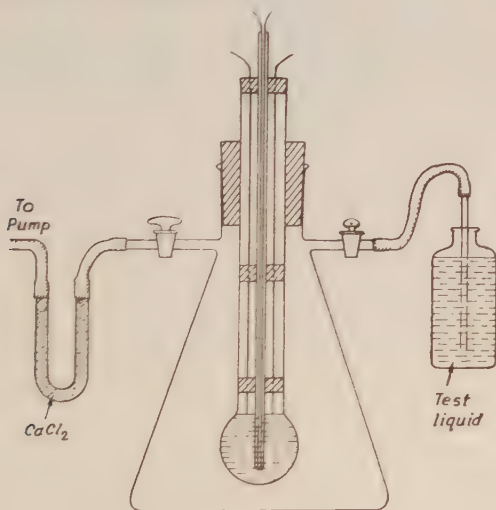


Fig. 2. Degassing arrangement.

3. To prevent bulk superheating as well as subcooled boiling of the test liquid a temperature regulating device was necessary. About half a litre of the test liquid was contained in a glass cylinder which was immersed in a bath of paraffin oil (Fig. 3). The temperature of the test liquid was kept within narrow

limits near the boiling point by regulating the temperature of the paraffin oil bath. Mercury-in-glass thermometers graduated to 0.1°C were used to indicate temperature.

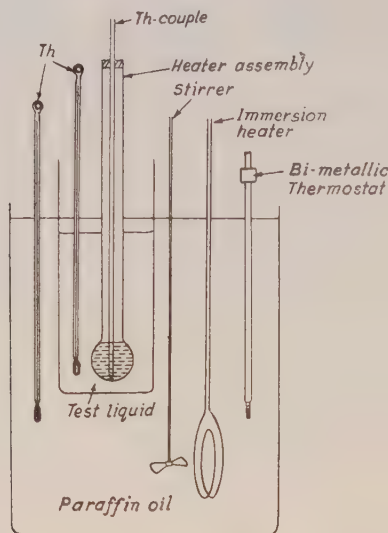


Fig. 3. Bath arrangement.

EXPERIMENTAL PROCEDURE

The heater bulb, annealed at 400°C over a period of 48 hours, was thoroughly washed with conc. sulphuric acid saturated with potassium dichromate and was then rinsed several times with water. The bulb thus cleaned was introduced into the degassing flask through a rubber cork fitting closely into its mouth. The flask was gradually evacuated to a pressure of about 10^{-3} mm. of mercury, and the mercury in the heater bulb was simultaneously heated to 200°C . The process was continued for an hour; the connection to the pump was then closed and the test liquid was drawn into the flask while the bulb was still hot so that the bulb surface could be covered with a thin layer of the test liquid before transferring it to the test bath. The flask was then brought close to the test bath and the heater assembly quickly transferred to it.

The liquid in the test bath (about 500 ml) was boiled off to two-thirds of the initial volume. The heater was then switched off and the sample was allowed to reach quiescence. After an interval of 16 to 20 hours the heater was again switched on and was adjusted to a series of gradually ascending step values (successive steps not differing by more than 2°C). The temperature of the bulk liquid was kept at the reference value, within a limit of 0.05°C ., for each value of the heat input by suitably adjusting the bath temperature. For any given heat input the heater bulb attained steady state within a minute. To ensure that

steady state readings were taken, about 5 minutes were allowed to elapse at each step before measurements were noted. Finally, a temperature was reached such that a slight increase in the heat input made the liquid film explode with an appreciable popping sound. It was noted that the loudness of the explosion increased significantly with the degree of superheat. The nucleation centres were innumerable and were found to be evenly distributed on the bulb surface. Within a few seconds of explosions the temperature of the mercury in the bulb suddenly dropped through 20° – 25°C and attained a steady lower value within a minute. Liquids with larger superheat values showed a larger temperature drop at this stage. During any set of experiment the liquid did not fall in level by more than a centimetre. The test bath beaker and the heater assembly were held in massive stands resting on compressed felt slabs to keep them free from vibration. The steady state temperature gradient from mercury to the liquid bulk is shown in Fig. 4.

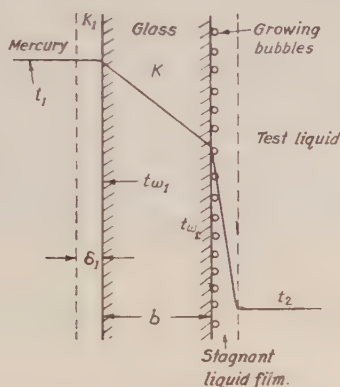


Fig. 4. Drop of temperature from mercury to test liquid.

CALCULATION OF MAXIMUM SUPERHEAT TEMPERATURE

At the steady state, assuming that heat is transferred across the stagnant mercury film wholly by conduction,

$$t_1 - t_{\omega_1} = \frac{\delta_1}{AK_1} Q \quad \dots (1)$$

$$t_{\omega_1} - t_{\omega_2} = \frac{b}{AK} Q \quad \dots (2)$$

where t_1 = bulk temperature of mercury, t_{ω_1} = inner wall temperature of the glass bulb, t_{ω_2} = outer wall temperature of the glass bulb, K_1 = conductivity of mercury, K = conductivity of laboratory pyrex glass, A = mean surface area of the glass bulb, b = mean wall thickness of the glass bulb, δ_1 = thickness of

the stagnant mercury film, Q = heat input at any steady state. Adding Eqs. (1) and (2), we have

$$t_1 - t_{\omega_2} = \frac{Q}{A} \left(\frac{\delta_1}{K_1} + \frac{b}{K} \right) \quad \dots(3)$$

But, $\delta_1 \ll b$ and $K_1 \gg K$ and $\delta_1/K_1 \ll b/K$. So Eq. (3) reduces to

$$t_{\omega_2} = t_1 - \frac{Qb}{AK} \quad \dots (4)$$

The value of t_{ω_2} at the highest steady state is noted as the maximum superheat temperature of a liquid.

RESULTS

More than twenty repeat tests were made with fresh samples for each of nine different organic liquids (carbon tetrachloride, chloroform, acetone, benzene, methyl alcohol, carbon disulphide, di-ethyl ether, *n*-pentane and ethyl bromide) allowing different intervals of standing between runs in order to achieve reproducibility of results. Reproducible values of the maximum superheat within the range of 5°C was attained when the boiled sample was allowed to stand overnight and the heat input to the bulb increased slowly. Any sudden fluctuation of the mercury temperature, even through 0.5°C., or a slight vibration of the support of the bulb assembly, was found sufficient to initiate nucleation at high liquid superheat.

The maximum superheat temperatures and the temperature drops (Eq. 4) are shown in Table I.

TABLE I

| Liquid | Boiling point °C | Mercury temperature °C | Temperature drop $\left(\frac{Qb}{AK} \right)$ °C | Maximum superheat temperature °C | Bulk temperature of the liquid °C | Superheat °C |
|----------------------|---------------------|---------------------------|--|-------------------------------------|--------------------------------------|-----------------|
| Carbon tetrachloride | 76.7 | 142 | 7 | 135 | 76.0 | 58 |
| Chloroform | 61.0 | 161 | 12 | 149 | 60.4 | 88 |
| Acetone | 56.5 | 188 | 23 | 165 | 56.5 | 108.5 |
| Benzene | 80.1 | 211 | 20 | 191 | 80.5 | 111 |
| Methyl alcohol | 64.0 | 211 | 29 | 182 | 65.0 | 118 |
| Carbon disulphide | 46.3 | 166 | 9 | 157 | 48.6 | 111 |
| Di-ethyl ether | 34.5 | 177 | 25 | 152 | 34.0 | 117.5 |
| <i>n</i> -Pentane | 36.1 | 142 | 10 | 132 | 35.2 | 96 |
| Ethyl bromide | 38.4 | 162 | 13 | 149 | 38.0 | 111 |

The values of A and b for the glass bulb used were measured optically. The conduction heat loss along the heater leads and the stem of the glass heater and the part of the I^2R wattage not absorbed by the mercury medium, added together, amounts to about 5% of the total heat input and so the value of Q taken was reduced by that amount. As regards the conductivity of glass, the standard value for laboratory brand of pyrex, type 475/636 as quoted by Jakob (6) (corrected for the mean temperature) has been taken.

DISCUSSION

The possible sources of error in our calculation of superheat might lie in the (1) measurement of the surface area of the glass bulb and its wall thickness and (2) estimation of the magnitude of the heat losses. It is estimated, however, that the error in superheat temperature due to uncertainties in these quantities would not exceed 3°C . at its maximum value.

The general agreement of the experimental values of superheat in the present case with those of Wismer *et al.* and the graph resulting from theoretical values

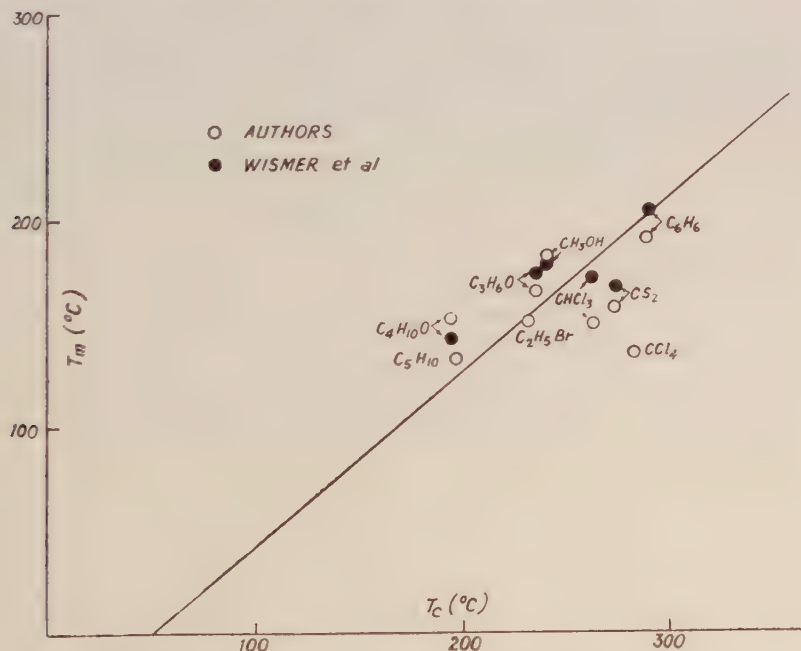


Fig. 5. Maximum superheat of liquids - comparison of results of the authors, and Wismer *et al.*, and deductions from Van der Waals equation.

T_m = Limiting temperature for existence of a liquid phase at atmospheric pressure
 T_c = Critical temperature.

Straight line $\frac{T_m}{T_c}$, deduced from Van der Waals equation.

is given in Fig. 5. Exact agreement can not be expected since the Van der Waals equation on which the theoretical curve is based is at best approximate only.

The fairly high values of superheat of the liquids obtained by the present method lend support to the contention that cavitation of the liquid film at the glass surface was initiated in the absence of gas nuclei at the interface. The divergence of the maximum superheat temperatures of different liquids from the theoretical curve seems to be due to their relative deviations from Van der Waals equation.

REMARKS

1. Since the liquid boundary film is superheated, the measurement of the superheat temperatures is not influenced in the present method by the presence of chemically inert moles in it.

2. Since cavitation takes place at the glass-liquid interface, the method offers special advantage for studying the effect of any variation of the nature of the interface on the superheat of liquids.

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Letters to the Editor

The Board of Editors will not hold itself responsible for opinions expressed in the letters published in this section. The notes containing reports of new work communicated for this section should not contain many figures and should not exceed 500 words in length. The contributions must reach the Assistant Editor not later than the 15th of the second month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors.

2

A NEW METHOD FOR MEASURING ABSOLUTE MAGNETIC SUSCEPTIBILITIES

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A coil carrying an electric current possesses a magnetic moment. If introduced in a magnetic field with its moment parallel to the field-direction, it will behave as a magnetic body. So, in a Curie-balance type set-up, if we place the sample inside the coil, then by adjusting the current, we can make the moment of the coil equal and opposite to the moment induced in the sample and the system will experience no translatory force.

The working formula can be shown to be

$$\chi = \frac{i - i_c}{i_s - i_c} \cdot \left(\chi_s - \frac{K_a}{\rho_s} \right) \cdot \frac{m_s}{m} + \frac{K_a}{\rho}$$

where

χ = mass-susceptibility of the sample

ρ = density of the sample

m = mass of the sample.

χ_s , ρ_s and m_s are the respective values for a standard substance.

K_a = volume susceptibility of air

i = current necessary to balance the force on the sample

i_s = same with the standard substance

i_c = current necessary to balance the force on the coil alone.

It is better to have a calibration curve by working with a number of different samples of known susceptibilities.

The advantages of the method over the older method are :

- (a) remote control eliminates manual rotation of torsion head, thus reducing the effects of vibration, etc.
- (b) since the balancing force is applied directly on the sample itself, no torsion on the suspension fibre is required and the system remains perfectly undisturbed.
- (c) electric currents can be very accurately measured.
- (d) the balance chamber can easily be made vacuum-proof and can be kept dry.

The method has been tried experimentally and the instrument was found to work satisfactorily. Details will be published later.

My thanks are due to Professor A. Bose for his kind interest in the work.

3

INTERMOLECULAR POTENTIALS OF H_2 AND D_2

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(Received April 12, 1961)

The importance of the quantum effects for H_2 and D_2 at low temperatures makes the determination of their potential energy functions very interesting. Further, it is likely to show whether their potential energy functions are the same, as it should be for two isotopes, provided their non-spherical nature may be neglected. Although it is known that there should be some difference in the inter-molecular potentials of H_2 and D_2 due to the difference in their zero-point energies, it was so long thought that this effect can be neglected (Mason and Rice, 1954). Moreover the earlier experimental data were not accurate enough to test this conclusively. Very recently Michels *et al.* (1960a) have determined the second and third virial coefficients of H_2 and D_2 by using a precise method (Michels *et al.* 1960b) utilising their compressibility data (Michels, *et al.* 1959) between the temperature range from -175°C to 150°C . They have observed that the force constants for H_2 and D_2 determined previously on the L—J (12 : 6) model cannot represent the virial data satisfactorily. Hence they have redetermined the force

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constants for H_2 and D_2 and have found them to differ from each other by more than what can be ascribed to be experimental errors. They have also considered the non-spherical nature of the potential energy functions to represent the virial data.

It was therefore considered desirable to have a more detailed investigation of the intermolecular potentials of H_2 and D_2 to test whether the results obtained by Michels *et al.* (1960a) are true for other potentials as well. We have thus fitted the second virial coefficient, $B(T)$, data of Michels *et al.* (1960a) to the exp-six model by taking into consideration the quantum effects. The results obtained are shown in Table I. In Table II the experimental and the calculated values of $B(T)$ are shown. For the sake of comparison the values calculated on the exp-six model from the force constants determined by Mason and Rice (1954), and those calculated by Michels *et al.* (1960a), are also shown.

It may be seen from the Tables I and II that the results obtained on the exp-six model confirm the finding of Michels *et al.* (1960a) that the force fields of H_2 and D_2 are not exactly the same. However, the agreement with the experimental data calculated on the exp-six model from the force constants determined by us is very good over the entire temperature range and hence further consideration of the non-spherical nature of the potentials may not be necessary.

TABLE I
Force parameters for H_2 and D_2 on the exp-six model

| Substance | Present work | | | Mason and Rice (1954) | | |
|-----------|--------------|----------------------|-------------------|--|----------------------|-------------------|
| | α | $\epsilon/k^\circ K$ | $r_m \text{ \AA}$ | α | $\epsilon/k^\circ K$ | $r_m \text{ \AA}$ |
| H_2 | 14.0 | 38.02 | 3.339 | 14.0 | 37.3 | 3.337 |
| D_2 | 14.0 | 37.33 | 3.334 | Assumed to be the same as those of H_2 | | |

It is to be noted that Michels *et al.* (1960a) could not find agreement in the whole temperature range with their force constants on L—J (12 : 6) potential model, within the experimental accuracy. Thus it appears that the exp-six potential model is an improvement over the L—J (12 : 6) model which has been already pointed out by Mason and Rice (1954).

Further work, by taking into consideration the third virial coefficient and the quantum corrections to the transport coefficients, is in progress.

The authors are grateful to Prof. B. N. Srivastava, D. Sc., F.N.I., for his valuable discussions.

TABLE II
Second virial coefficient for H₂ and D₂ in cm³ mole⁻¹

| T°K | Hydrogen | | | | Deuterium | | |
|-----|--------------------------|--------------------------|--------------------------------------|-------|--------------------------|--------------------------------------|-------|
| | Calculated | | | Expt. | Calculated | | Expt. |
| | Exp-6 present work | Exp-6 Mason & Rice | L-J(12-6) Michel <i>et al.</i> | | Exp-6 present work | L-J(12-6) Michel <i>et al.</i> | |
| 98 | -3.14 | | -3.16 | -3.06 | -4.48 | -4.35 | -4.59 |
| 103 | -1.69 | | -1.76 | -1.69 | -2.93 | -2.84 | -3.03 |
| 113 | +0.62 | | 0.68 | 0.67 | -0.38 | -0.30 | -0.38 |
| 123 | 2.79 | 3.34 | 2.71 | 2.63 | 1.78 | 1.78 | 1.79 |
| 138 | 5.18 | | 5.10 | 5.01 | 4.38 | 4.29 | 4.38 |
| 153 | 7.05 | | 6.95 | 6.89 | 6.26 | 6.19 | 6.36 |
| 173 | 9.01 | 9.27 | 8.82 | 8.84 | 8.25 | 8.20 | 8.37 |
| 198 | 10.66 | | 10.60 | 10.65 | 10.22 | 10.07 | 10.20 |
| 223 | 12.06 | 12.24 | 11.93 | 11.98 | 11.52 | 11.45 | 11.53 |
| 248 | 12.99 | | 12.95 | 12.97 | 12.54 | 12.51 | 12.53 |
| 273 | 13.73 | 13.93 | 13.75 | 13.76 | 13.31 | 13.34 | 13.30 |
| 298 | 14.36 | 14.51 | 14.40 | 14.38 | 13.98 | 14.00 | 13.90 |
| 323 | 14.86 | 14.97 | 14.92 | 14.87 | 14.46 | 14.53 | 14.38 |
| 348 | 15.22 | 15.34 | 15.34 | 15.27 | 14.87 | 14.97 | 14.76 |
| 373 | 15.59 | 15.63 | 15.69 | 15.60 | 15.27 | 15.33 | 15.07 |
| 398 | 15.86 | 15.88 | 15.97 | 15.86 | 15.41 | 15.63 | 15.33 |
| 423 | 16.05 | 16.07 | 16.21 | 16.08 | 15.62 | 15.87 | 15.54 |

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BOOK REVIEW

INTRODUCTION TO PHYSICAL CHEMISTRY, VOL. III. by S. N. Mukherjee
Art Union, Calcutta. 832 pages, ix. 1960(?) Price Rs. 25/-.

The third volume of Introduction to Physical Chemistry by Prof. S. N. Mukherjee, is intended for the post-graduate students of Indian universities. It is an advanced treatise divided into eleven chapters dealing with kinetic theory of gases, chemical thermodynamics, quantum theory and quantum mechanics, statistical mechanics and structure of molecules. In a book like this where a variety of topics has to be treated it is probably not easy to maintain a balance in the matter of emphasis given to one topic or the other. However, this volume is to be read along with its companion volumes, particularly volume II. Together with the preparatory chapter on electromagnetism more than two-fifths of the book are devoted to quantum theory and quantum mechanics. But the section on the theory of electrolytes has been very meagrely treated without reference to its recent developments. The same remark applies to the theory of reaction rates. It is gratifying that most of the topics have been presented clearly without sacrificing rigour and accuracy. The author's long experience as a teacher of physical chemistry has naturally helped him to keep the conceptual difficulties of students in mind.

The book is not, however, free from drawbacks. Some of them the reviewer would like to point out here hoping that they may be given consideration while preparing a future edition of it.

The chapters on electromagnetism and on relativistic mechanics, particularly the former, could be reduced in size to the necessary minimum. Quite a number of topics in the chapters on chemical thermodynamics, structure of molecules, and even in the most exhaustively treated chapters on quantum theory and quantum mechanics have been dealt with too briefly. The author has given on several occasions alternative derivations of certain formulae. Some of them are no doubt instructive but become too discursive in an advanced treatise like this. What the author could have done was to prepare suitable problems at the end of each chapter based on these alternative deductions. In fact, this is a valid complaint of the reviewer that the author has not thought it necessary to incorporate a large number of problems including numerical ones as he did in earlier volumes of this treatise. In this way some portions of the book could go in the form of problems thus reducing its bulk to a reasonable size. Again in some of the deductions the number of steps written could easily be curtailed. Similar types of deductions have also been unnecessarily repeated. Portions of the book

dealing with mathematical operations proper, viz., algebra of operators, polynomials, etc., could have gone as appendices.

As written, the book has emphasised more fully on the theoretical aspects, derivation of equations, etc., but the experimental side could have been developed a little further.

A number of authors have been mentioned by name and their work has also been described, but there is hardly any reference, except in a few cases, to books or journals where the work referred to may be read in greater detail and in original.

Printing mistakes abound but except in a few instances none of them are particularly harmful.

Although the number of lines written in connection with the drawbacks have exceeded those written in its appreciation the reviewer must admit that he has enjoyed reading some of the chapters, and it is hoped that the teachers and students alike will find the book useful to them.

S. K. M.

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CONTENTS

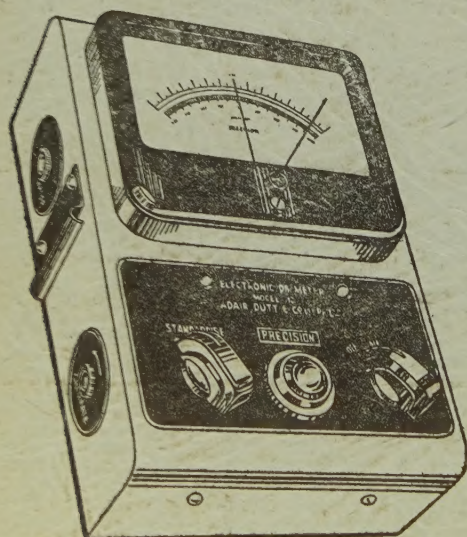
Indian Journal of Physics

Vol. 35, No. 6

June, 1961

| | PAGE |
|--|------|
| 30. Thermodynamic Properties of Fluid Flow Across a Magnetic Field— I. J. Singh and K. P. Chopra | 271 |
| 31. Scattering of Electrons by a Screened Coulomb Field in Higher Born Approximation— T. K. Mitra | 278 |
| 32. Fluorescence Spectra of Some Uranyl Salts— K. V. Narasimham | 282 |
| 33. A General Treatment of Penetration Factor in Alpha-Decay— S. K. Dutta ... | 299 |
| 34. Intensity Measurements in Molecular Bands— N. R. Tawde, B. G. Jyoti and M. I. Savadatti | 307 |
| 35. On the Superheat of Liquids— D. B. Sinha and A. K. Jalaluddin | 311 |
| LETTERS TO THE EDITOR | |
| 2. A New Method for Measuring Absolute Magnetic Susceptibilities— P. K. Ghosh | 319 |
| 3. Intermolecular Potentials of H_2 and D_2 — I. B. Srivastava and A. K. Barua ... | 320 |
| BOOK REVIEW | 323 |

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